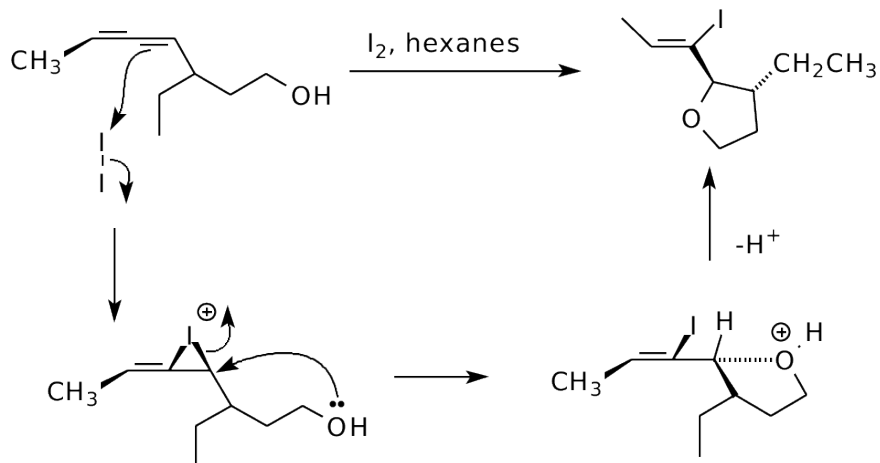


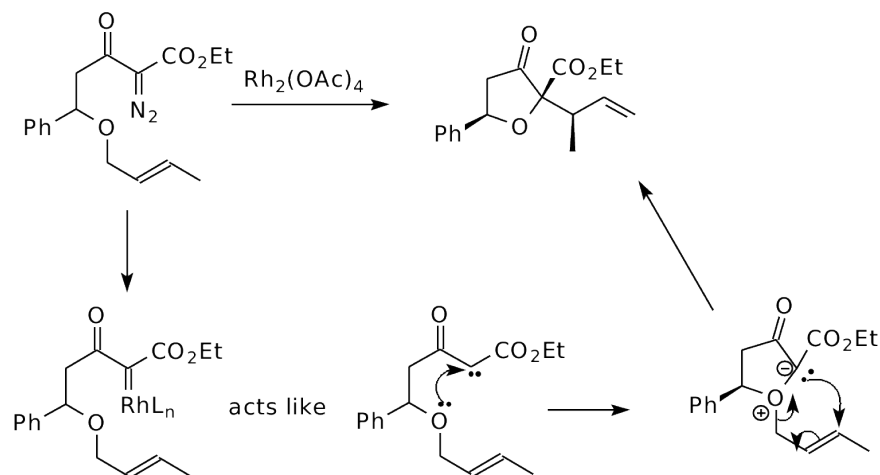
CH630
 Final Exam
 Key
 December, 2008

1. A.



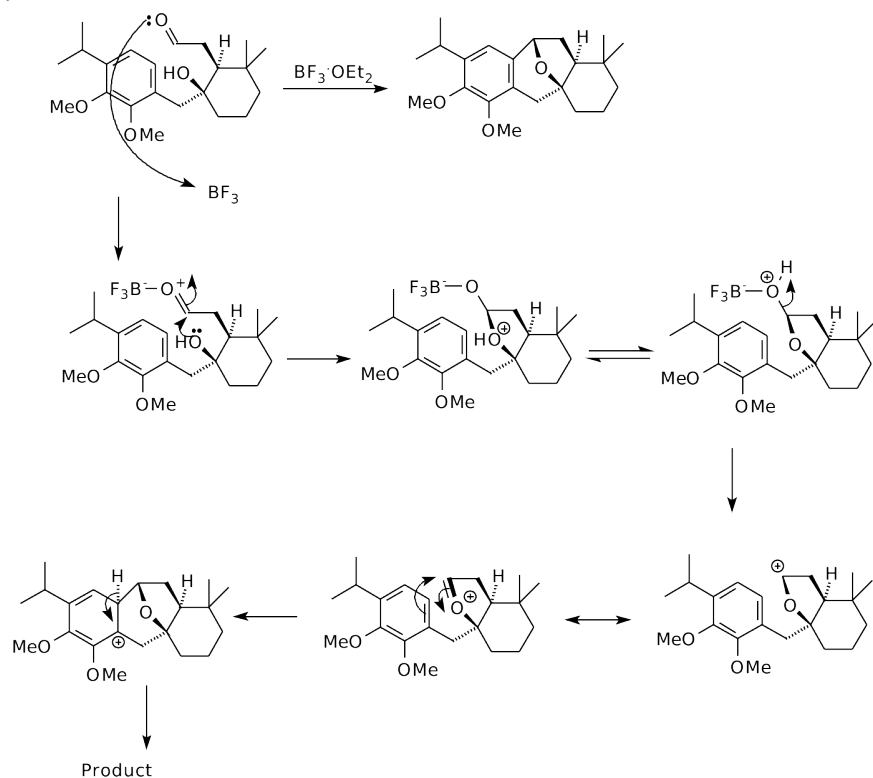
Electrophilic addition to one double bond; neighboring group participation by I to form iodonium ion; nucleophilic attack (5-exo-tet).

B.



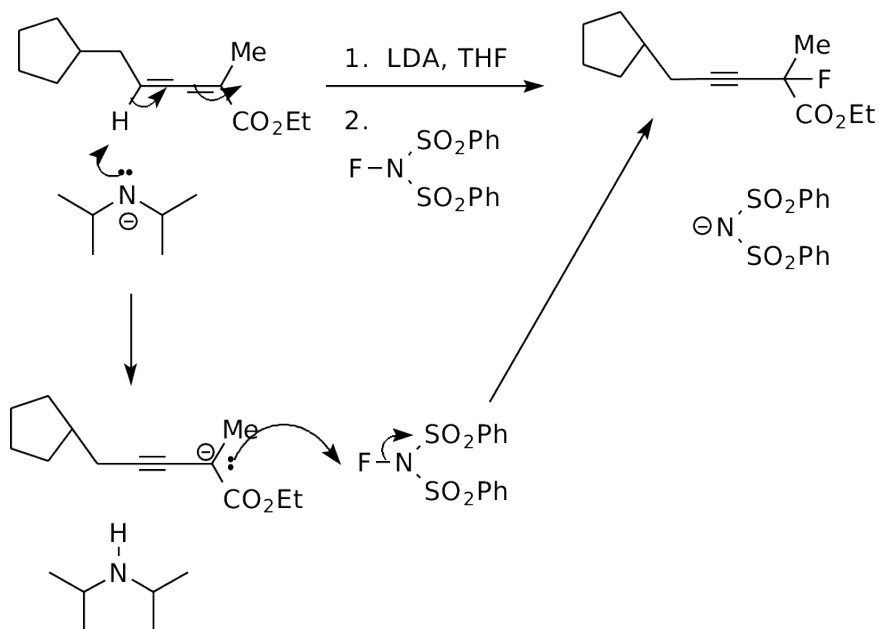
Carbenoid is electrophile; oxygen attacks to give an ylid; S_N2' attack (actually a pericyclic [2,3] shift, but given the polarity of the ylid, a debatable point).

C.



BF_3 is a strong Lewis acid. The carbonyl oxygen is most basic. One could reverse the steps for the hemiacetal formation/Friedel Crafts alkylation, but the reactant is probably a hemiacetal to begin with.

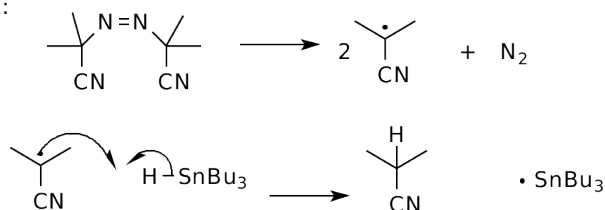
D.



Deprotonation of the vinyl proton leads to a stabilized enolate; the fluorine reagent is a formal source of F^+ because of the stabilization of the electron pair on N by the two sulfonyl groups.

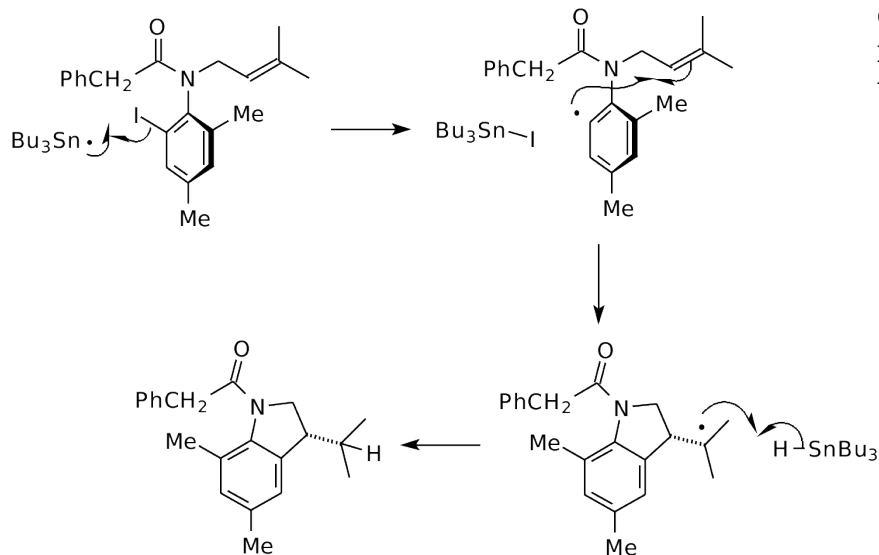
E.

Initiation:



A radical chain mechanism; iodine atom transfer followed by addition to the alkene.

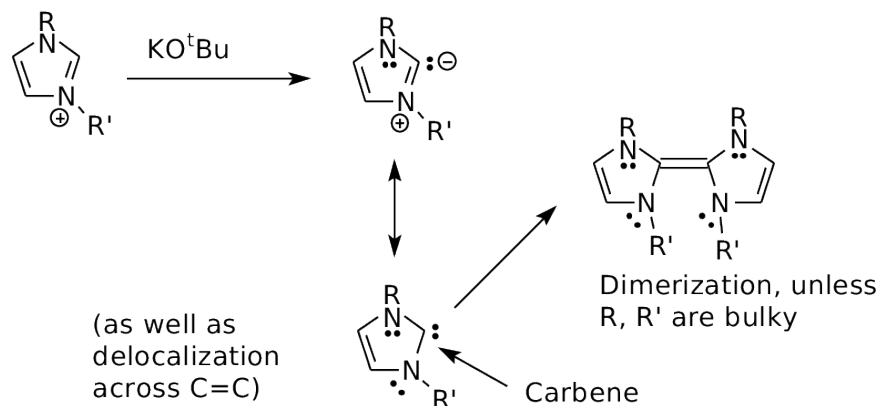
Propagation:



You need to show the initiation steps for full credit, but I will not take off for omitting the termination.

Termination: Radical recombination and/or disproportionation

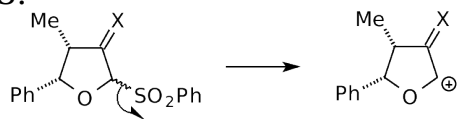
2.



Deprotonation between the nitrogens leads to a neutral species with significant carbene character. If R, R' are bulky, the aromatic character of the ring (and actually, the two nitrogen lone pairs are enough) fills the vacant p orbital, while the two electronegative nitrogens stabilize the carbon lone pair.

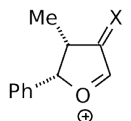
In the absence of steric blocking, dimerization occurs. If R, R' are big enough, these species can be isolated.

3.

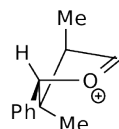


H = Me+H or CH₂

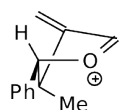
Stabilized carbocation; OK under relatively non-basic conditions



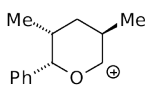
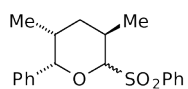
Side views:
(exaggerated)



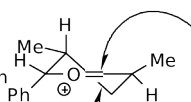
Both faces hindered to some extent
Low stereoselectivity.



Only one face blocked. Clear preference for attack from the top.



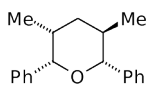
More stable conformation



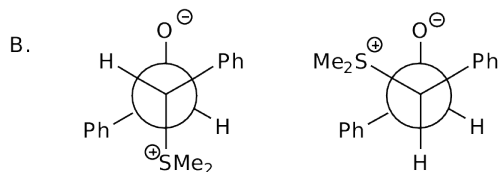
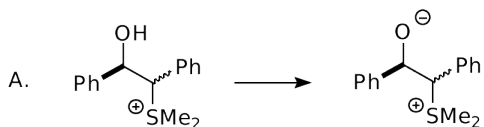
Top face attack = twist-boat TS
Disfavored

PhZnBr

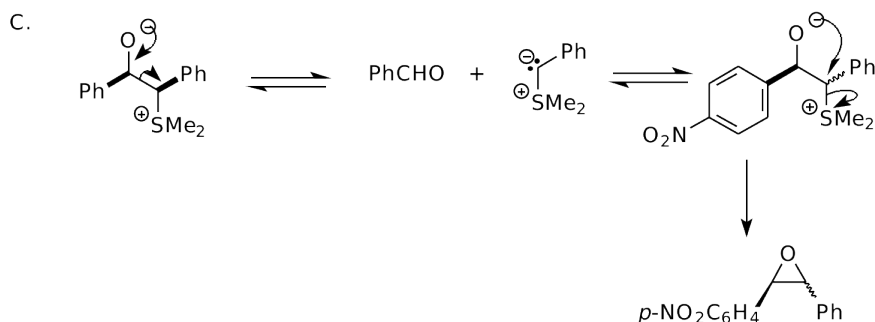
Bottom face attack = chair TS
Favored



4.



(controlled by Ph-Ph steric repulsion in gauche conformer)



Ring closure competes with fragmentation, because the orientation of the nucleophile and leaving group are poor for closure of the epoxide.

D. Ring closure is faster than fragmentation.

E. The temptation is to say that the fragmented ylide exchanges with D_2O . However, that would lead to equal portions incorporation into the two isomeric product epoxides from the syn, and this is not seen.

Deprotonation of the unfragmented reactant (internally, by the alkoxide?) leads to an ylide. The lifetime of this, compared to proton exchange and ring closure rates, will determine the extent of deuterium incorporation.

If ring closure from the anti isomer is fast, no exchange will occur.