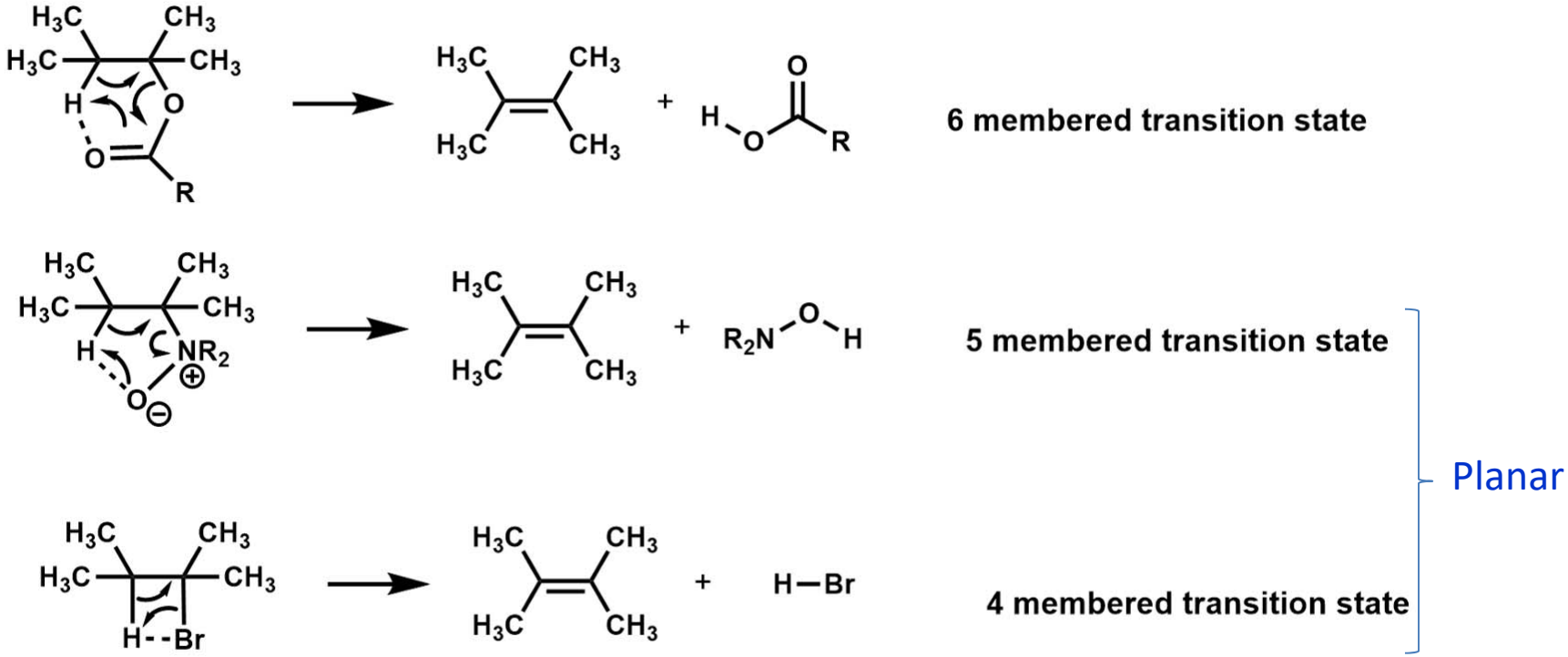
Syn 1,2 elimination

E_i (Elimination Internal/Intramolecular)

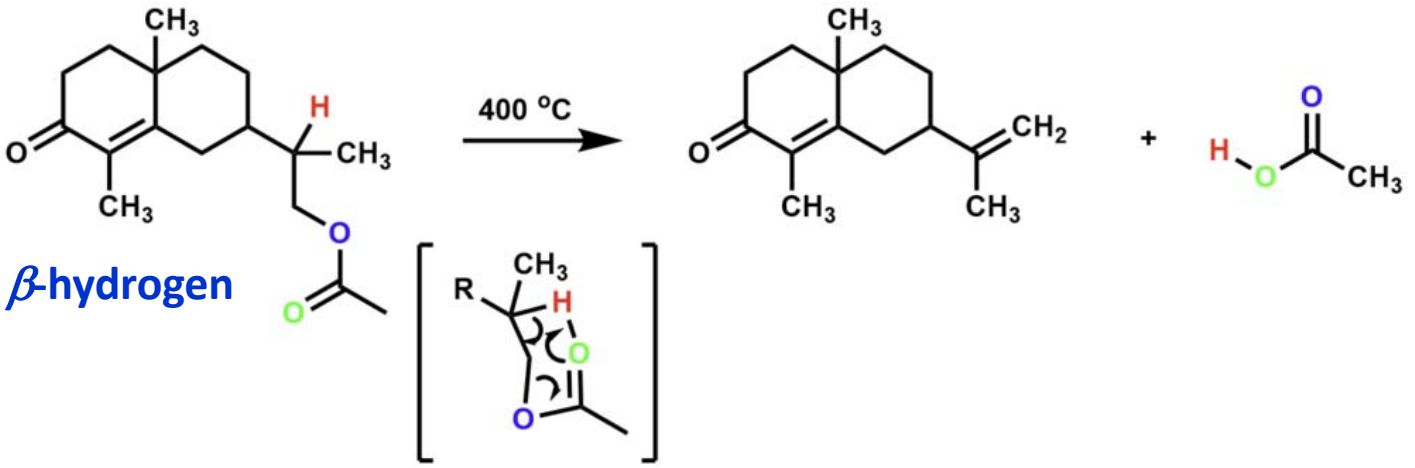
Thermal or Pericyclic Syn-eliminations

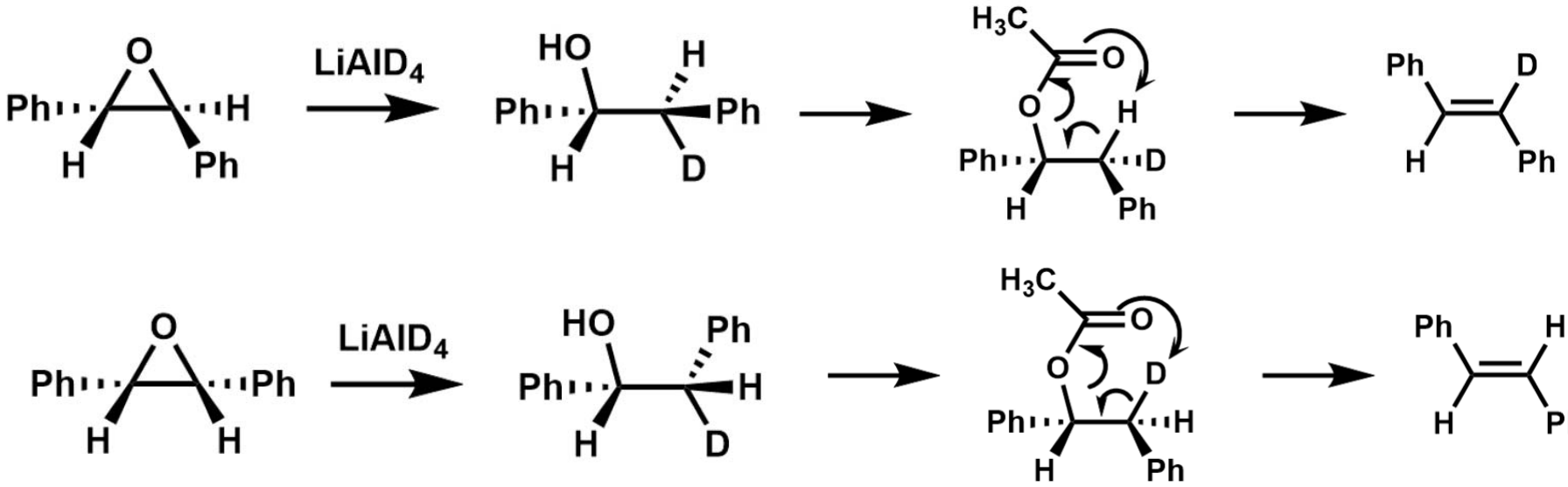
Cyclic Transition States

- Thermally activated, pyrolysis
- No additional reagents required
- No Intermediates
- Reaction kinetics shows first order
- Addition of Free radical inhibitors doesn't have any effect on the reaction



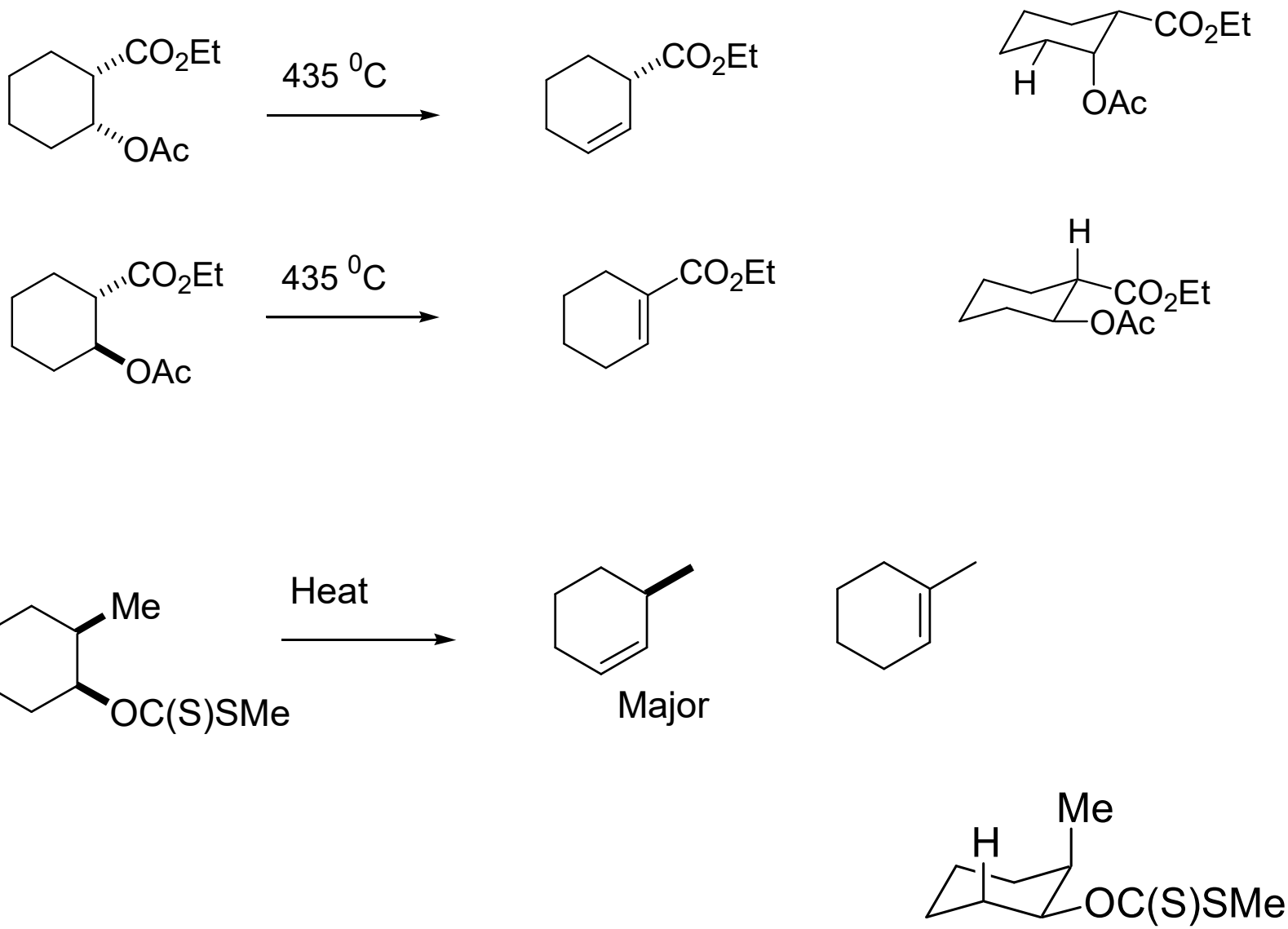
Ester Pyrolysis (~400 °C)



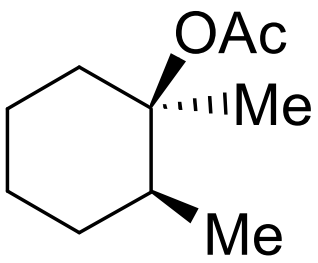


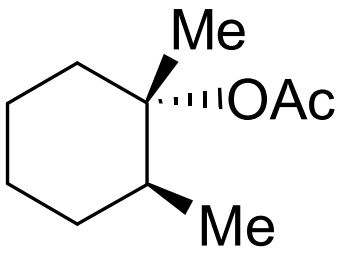
Isotopic labeling confirms that *syn* elimination occurs during ester pyrolysis in the formation of stilbene.

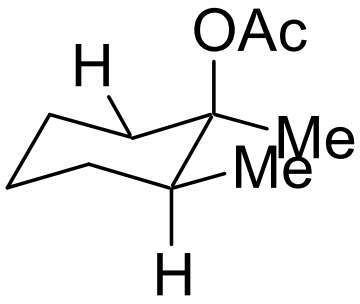
Syn –β elimination of acetates; pyrolytic elimination

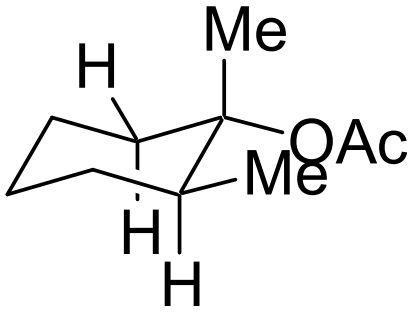


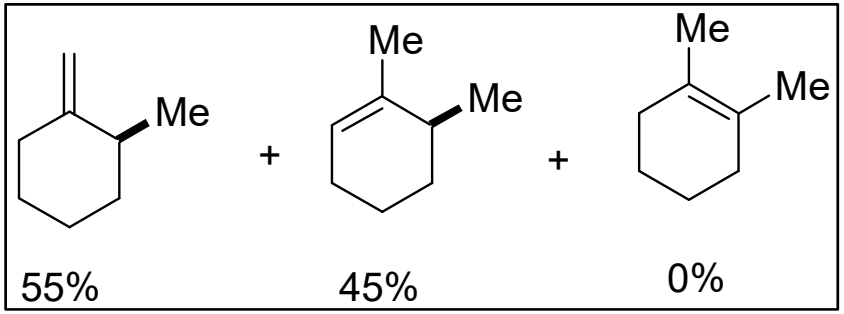
Syn –β elimination of acetates; pyrolytic elimination

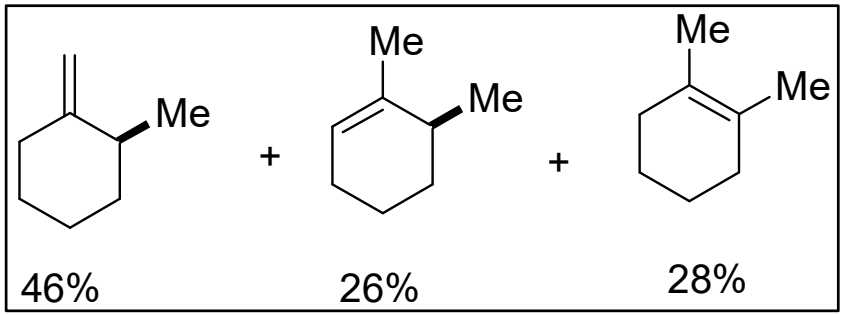








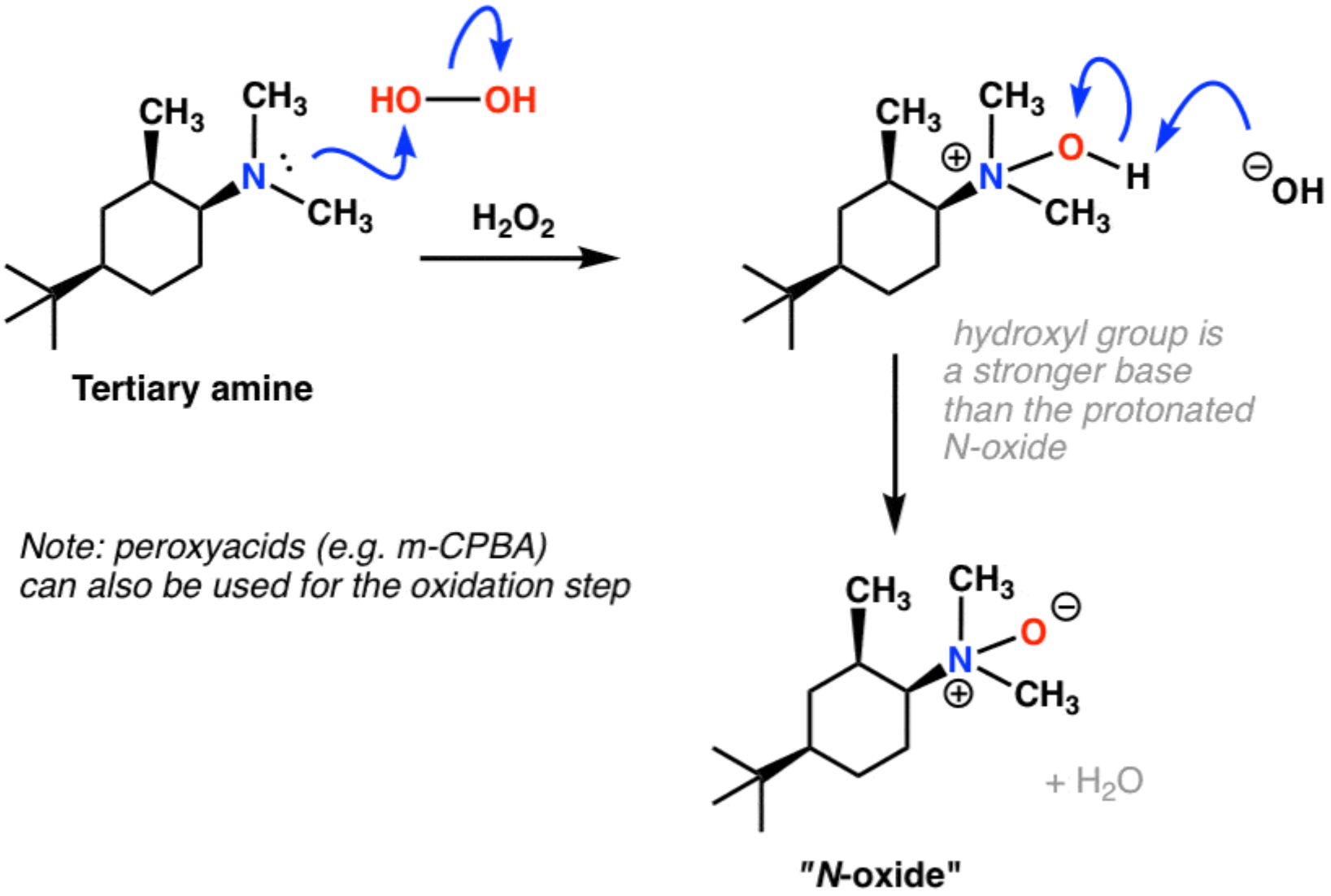




Syn –β elimination of N-oxide

The Cope Elimination

Step 1: Oxidation of a tertiary amine to an *N*-oxide

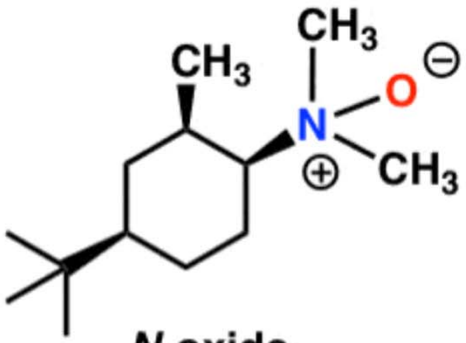


Note: peroxyacids (e.g. m-CPBA) can also be used for the oxidation step

Syn –β elimination of N-oxide

The Cope Elimination

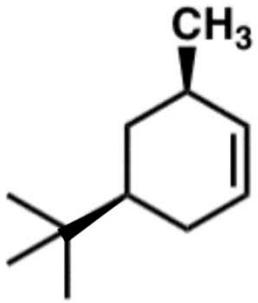
Step 2: Heat-induced elimination



N-oxide

Δ

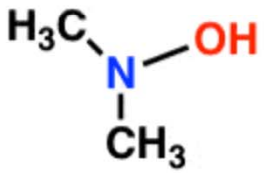
(heat)



Alkene

Bonds Formed	Bonds Broken
C–C (π)	C–H
O–H	C–N

\+

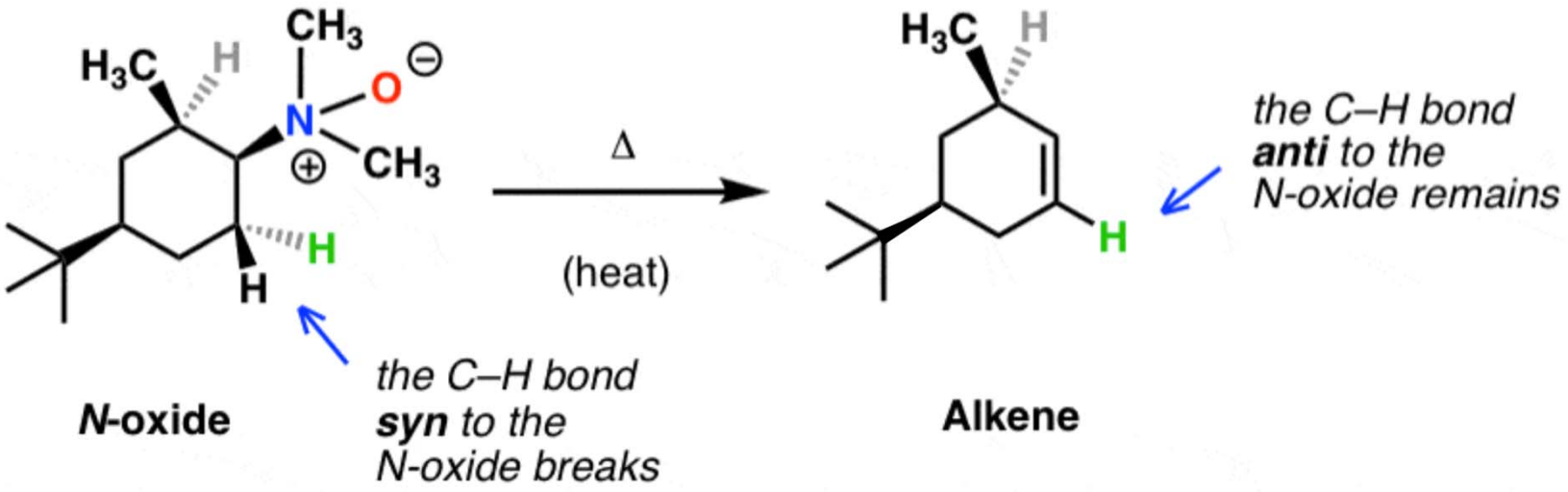


hydroxylamine

Syn –β elimination of N-oxide

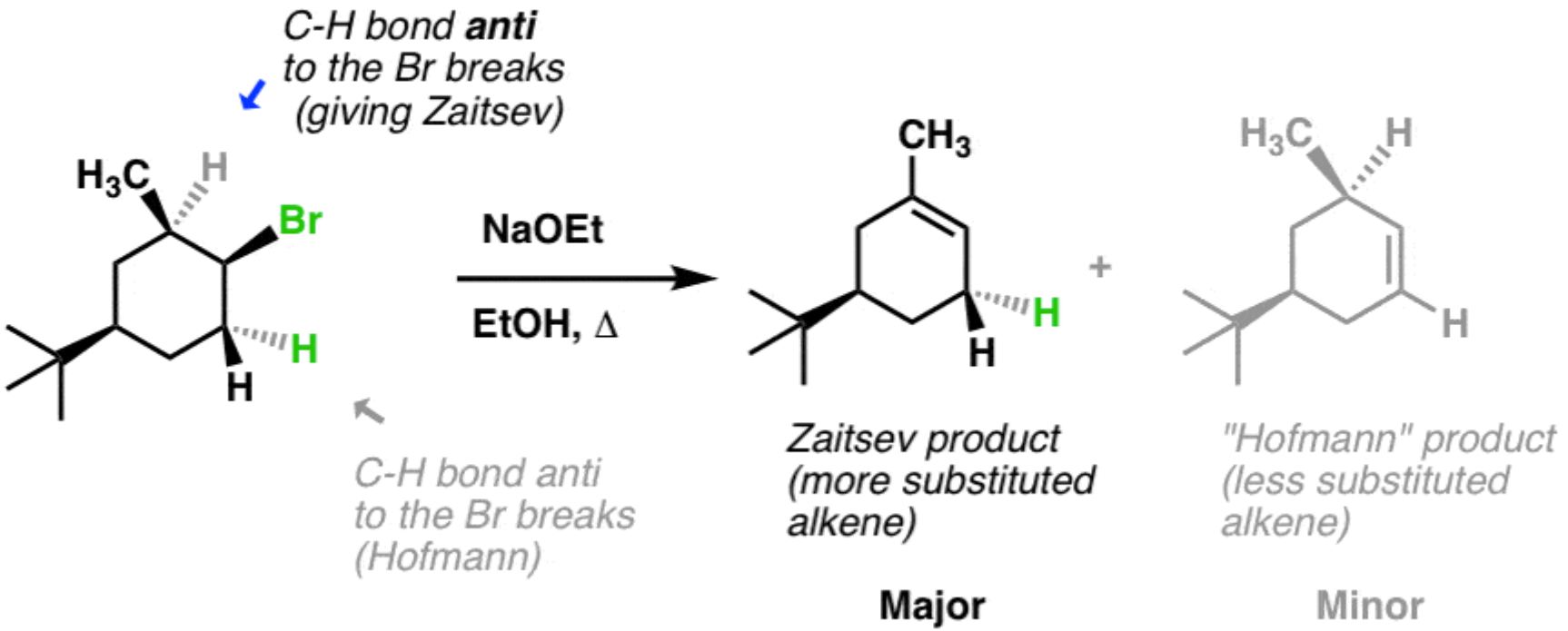
The Cope Elimination is an intramolecular "*syn*" elimination:

- *intramolecular*, in that the base and acid are on the same molecule
- *syn* , in that the the leaving group and acid are oriented on the same side of a C–C bond (in the *syn*- conformation)

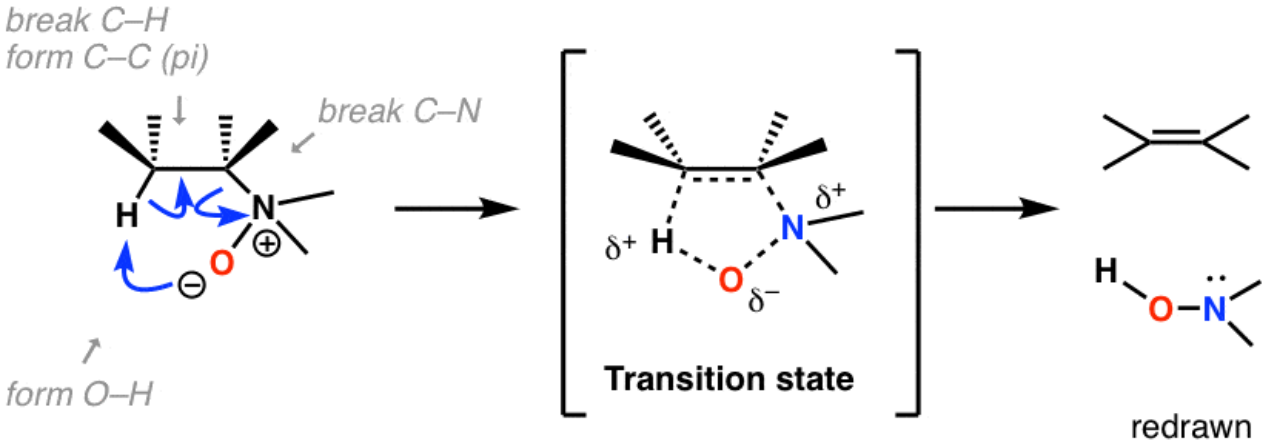


Syn –β elimination of N-oxide

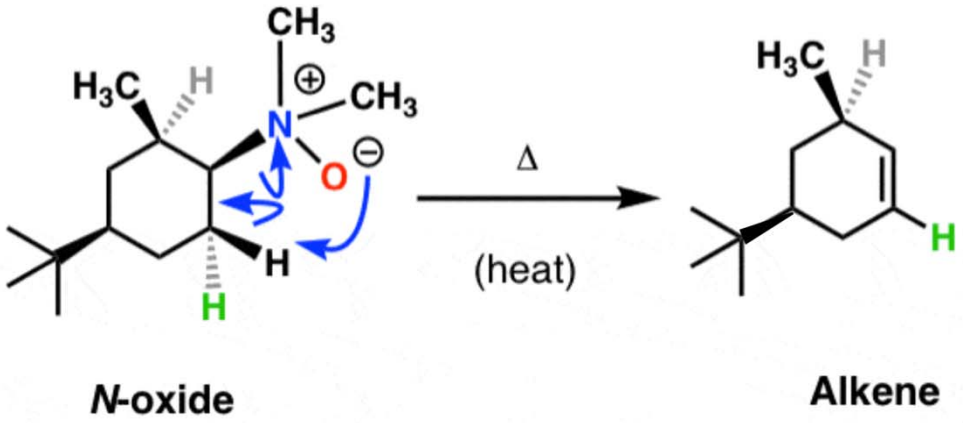
The E2 is an *anti* elimination (and almost always intermolecular)



The Cope Elimination proceeds through a concerted *syn*- elimination:



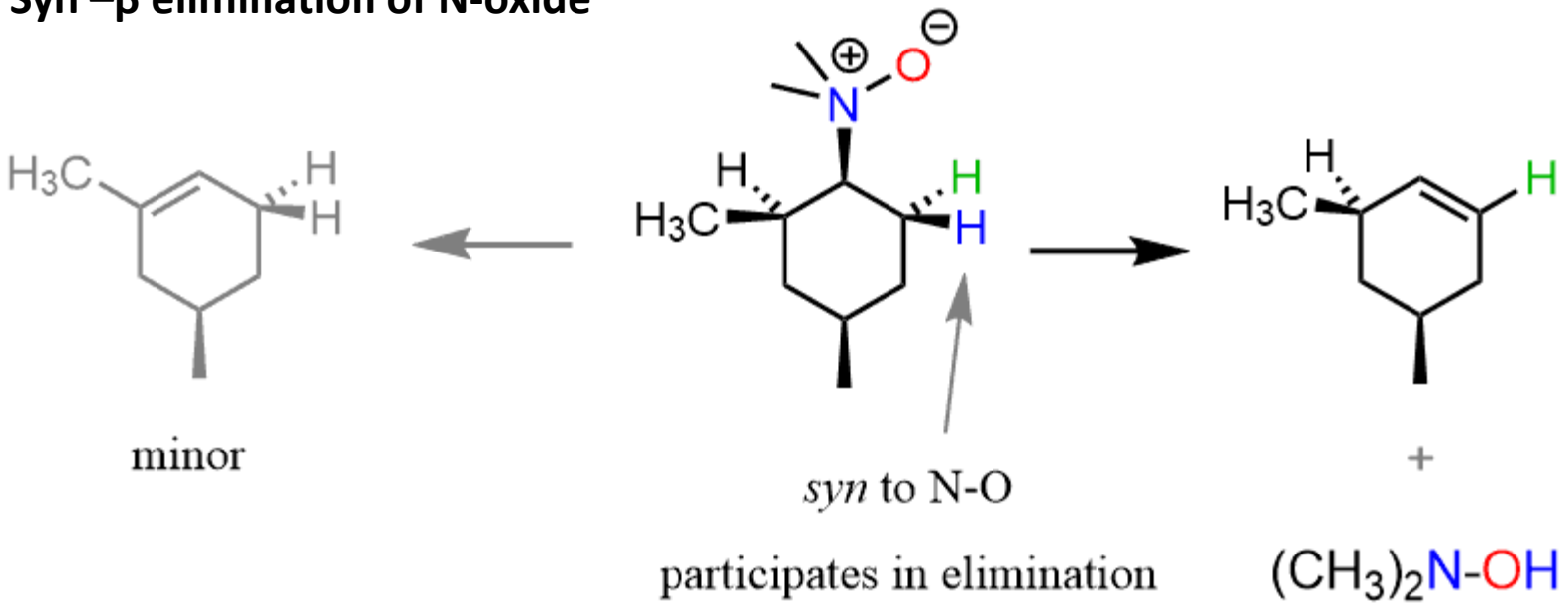
Cope Elimination: Mechanism

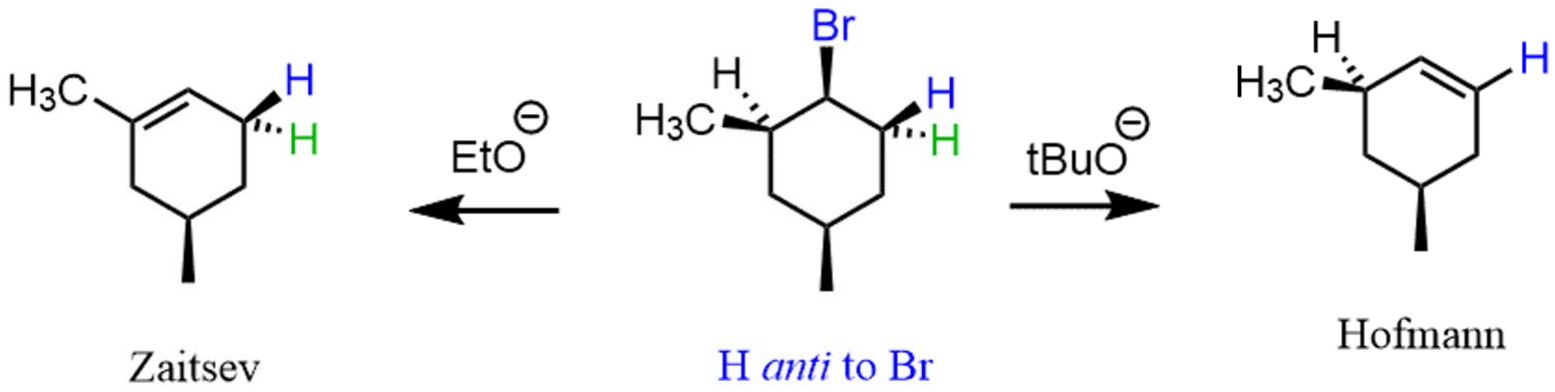


Bonds Formed	Bonds Broken
C–C (pi)	C–H
O–H	C–N

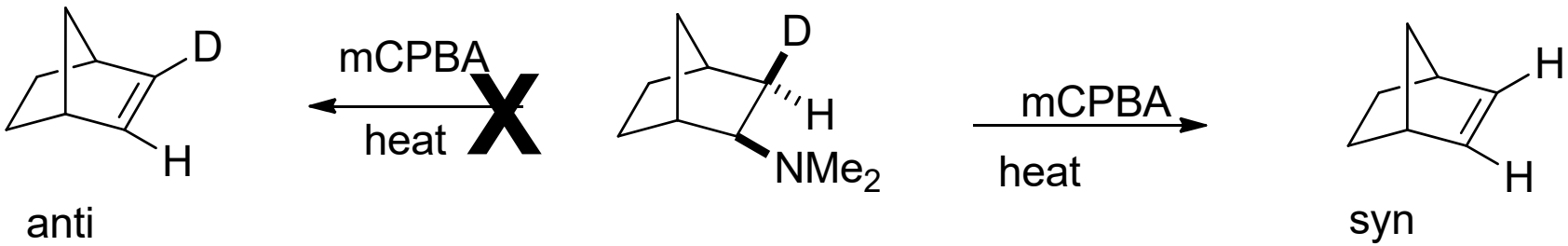
Syn –β elimination of N-oxide

Syn –β elimination of N-oxide

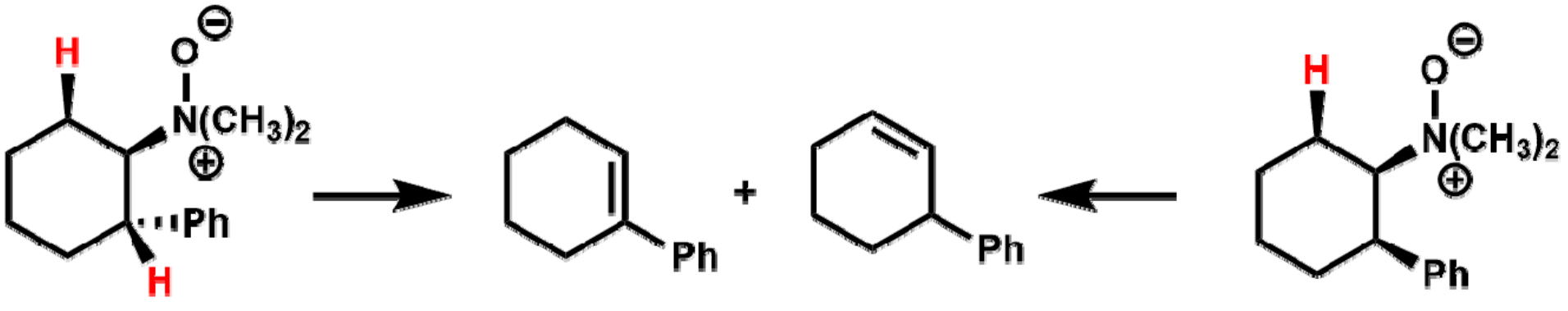




Syn –β elimination of N-oxide

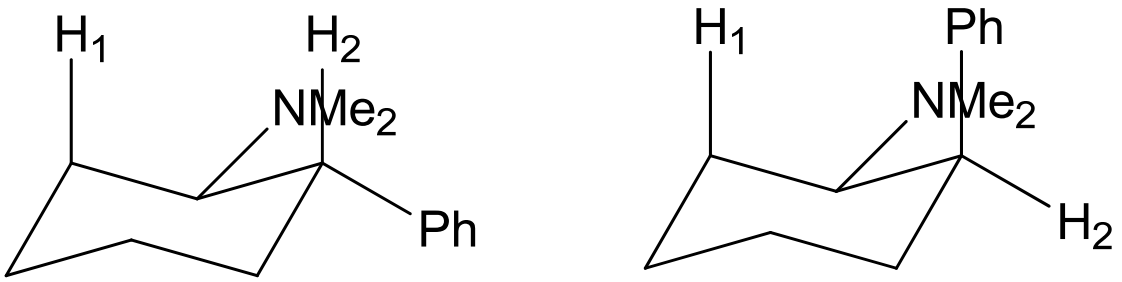


Syn –β elimination of N-oxide

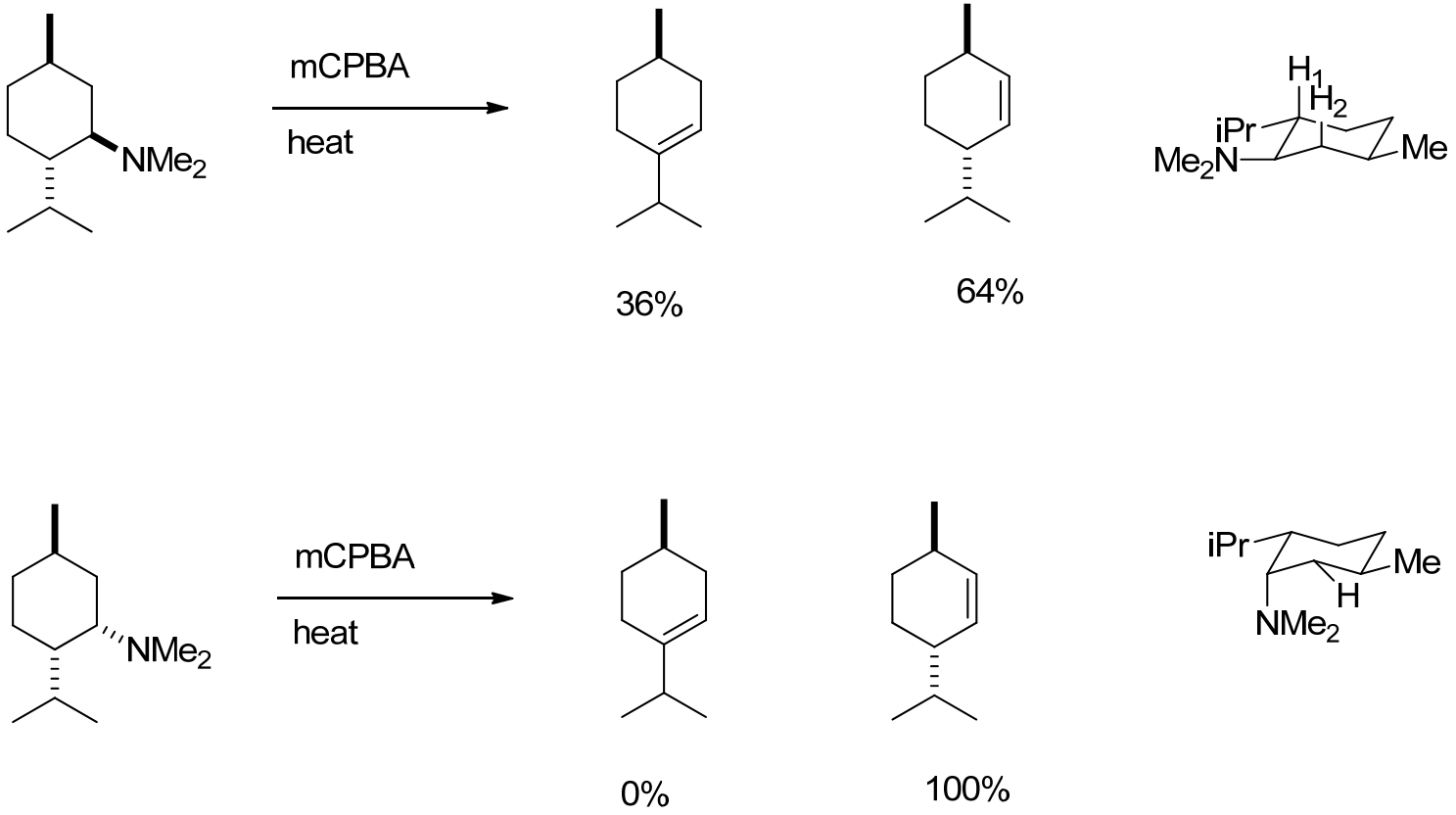


trans *cis*

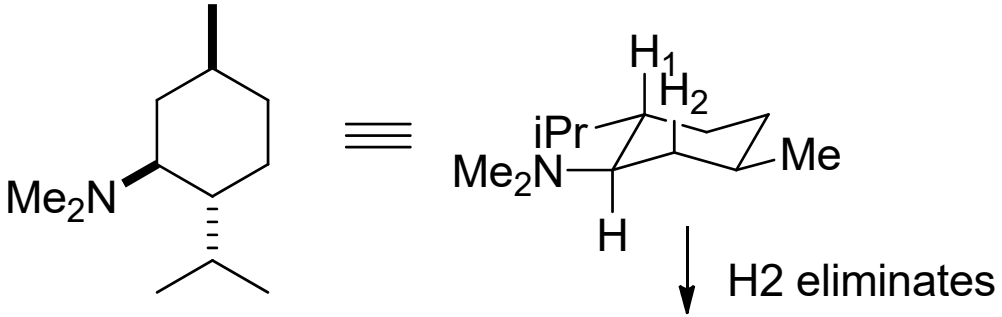
from *trans*	**85**	:	**15**
from *cis*	**2**	:	**98**

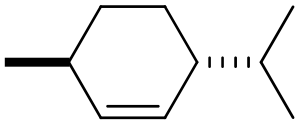


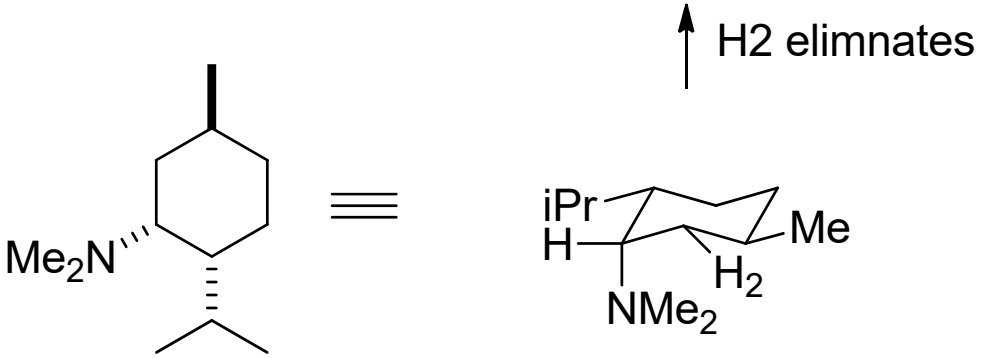
Syn –β elimination of N-oxide



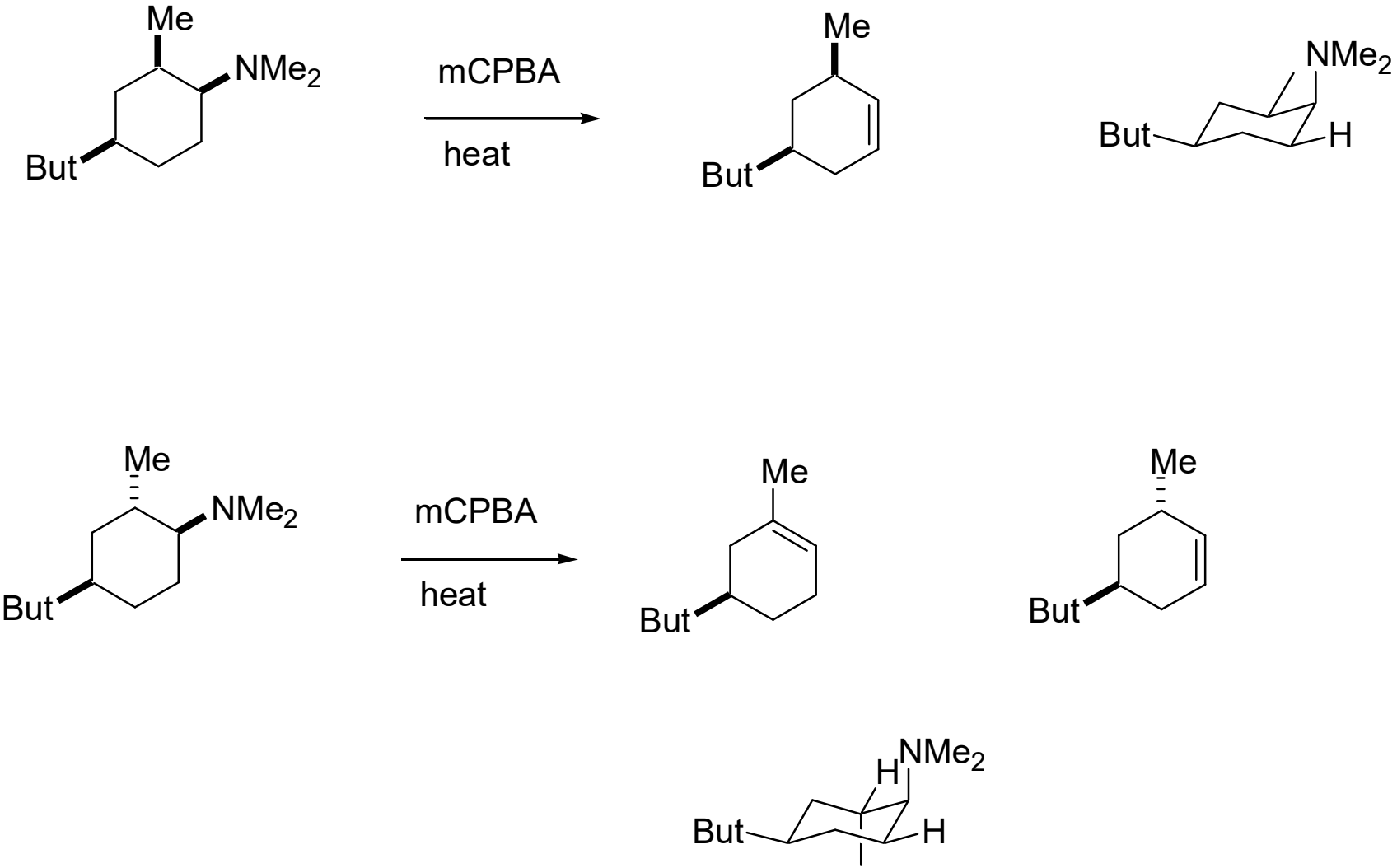
Syn –β elimination of N-oxide





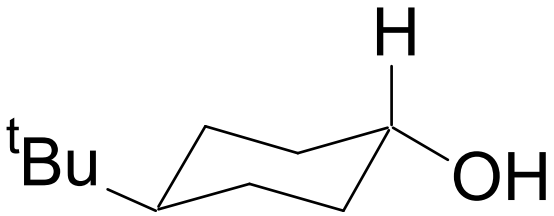


Syn –β elimination of N-oxide

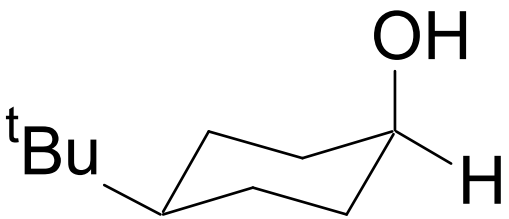


Explain the relative rate differences?

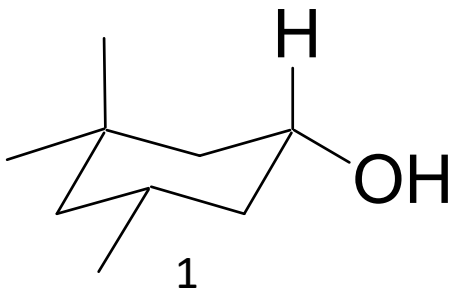
Relative rates of chromic acid oxidation



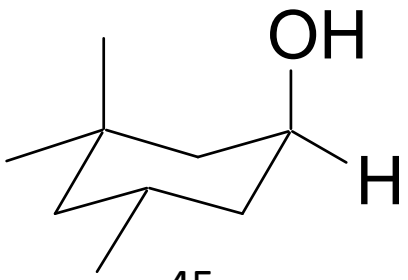
1



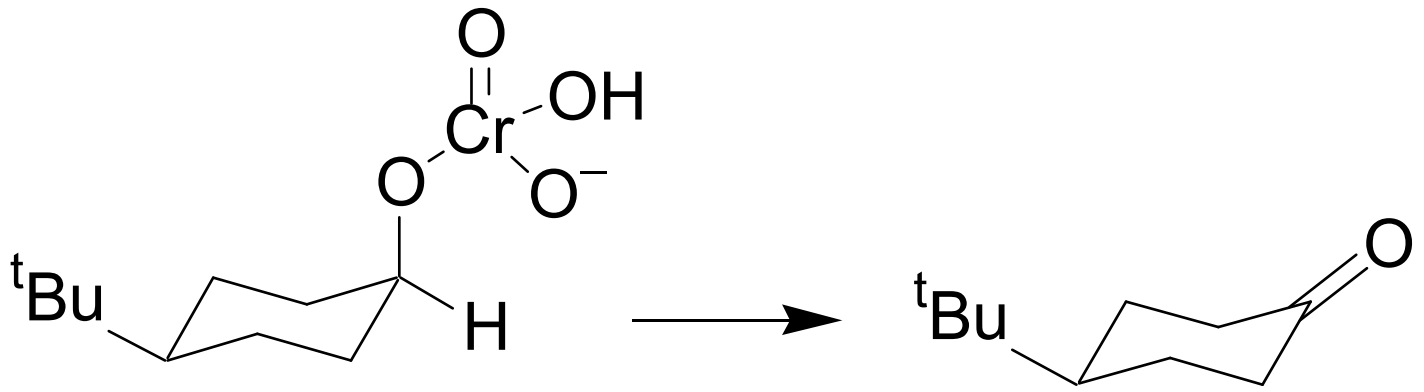
3.2

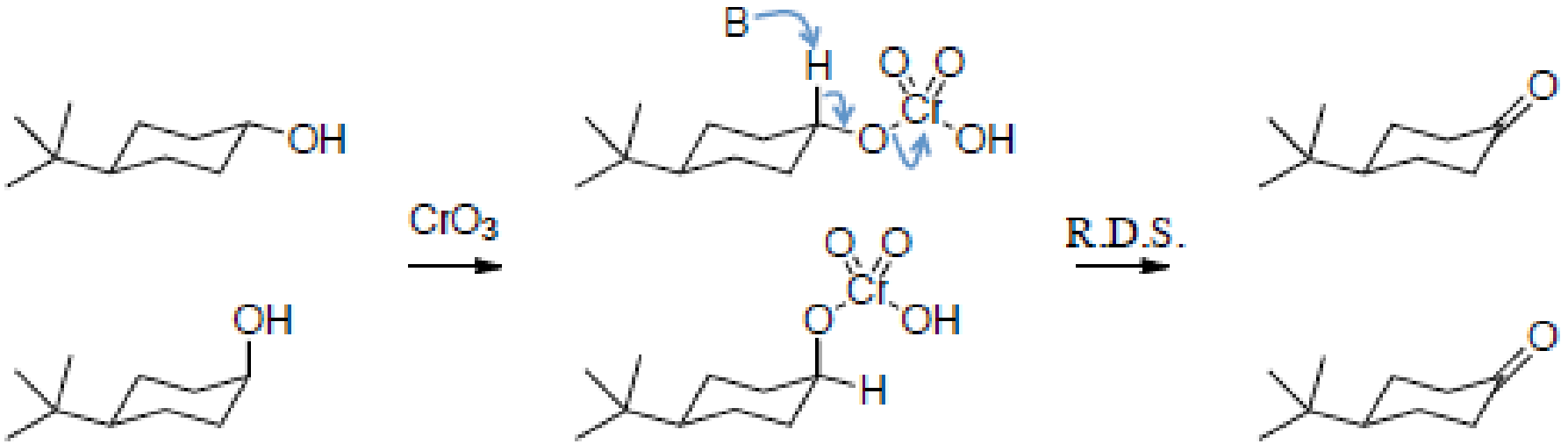


1

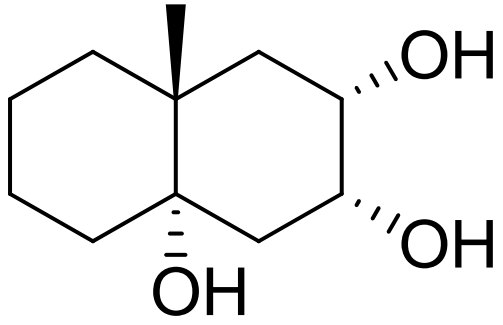


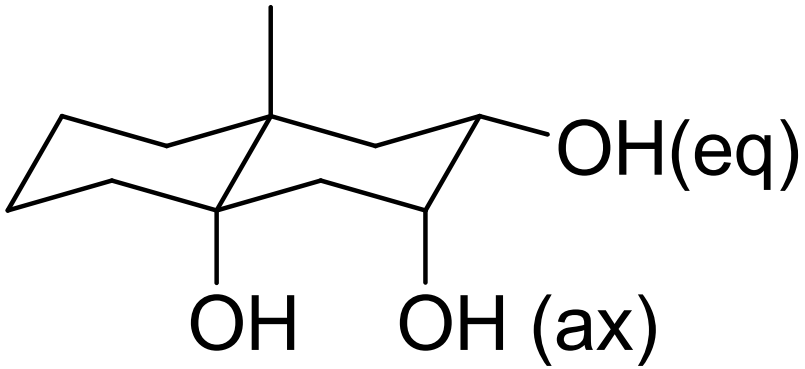
45


O
Cr
OH
O
O⁻
tBu
H
tBu
O


OH
CrO3
OH
B
H
O
O
Cr
O
OH
O
O
Cr
O
OH
H
R.D.S.
O
O

Which of the “OH” group in the following compound will oxidize rapidly in presence of PCC. Explain your answer with proper reasoning?

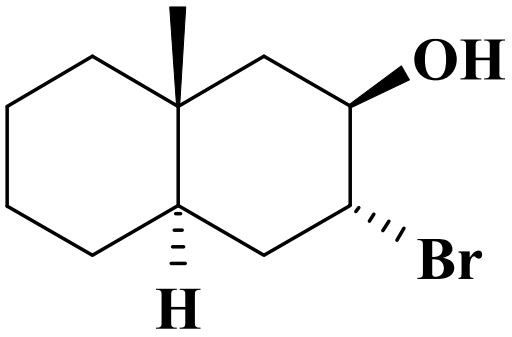




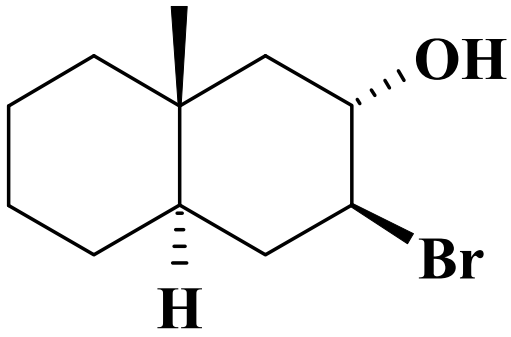
The secondary axial alcohol will be oxidized first.

Which of the following compound will be faster reacting under the given reaction condition?

Problem: Which of these two compounds would form an epoxide on treatment with base?

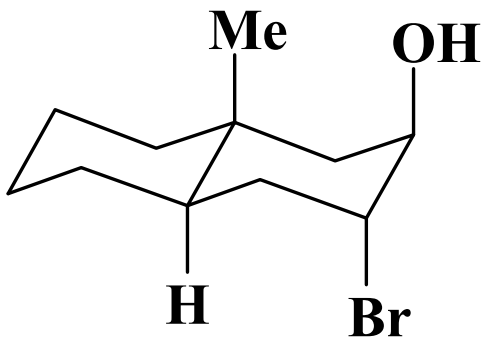


A

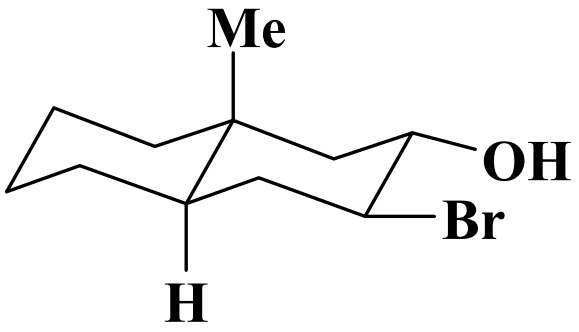


B

Hint:

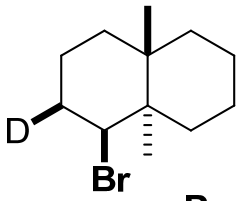


A



B

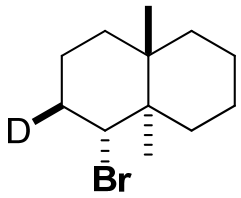
Q. Explain the following reaction with proper explanation



P

NaOEt/EtOH

Olefin with all "D" retained



Q

NaOEt/EtOH

Olefin with all "D" lost