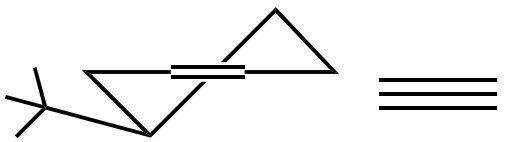
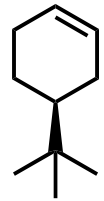
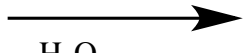
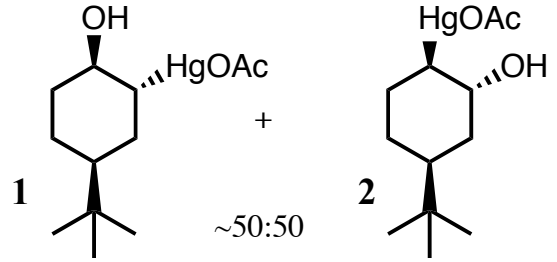
Oxymercuration



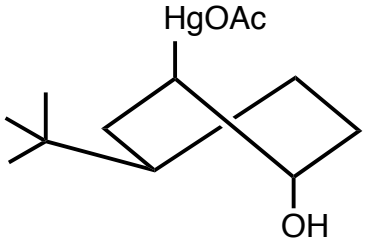


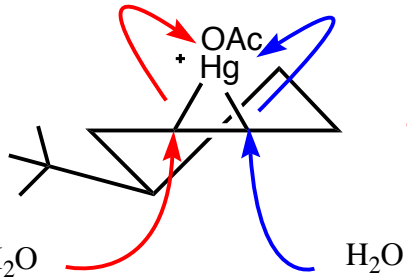
racemic

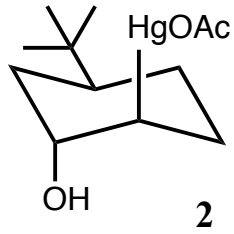




Total of 8 racemates possible. Only 2 are formed.

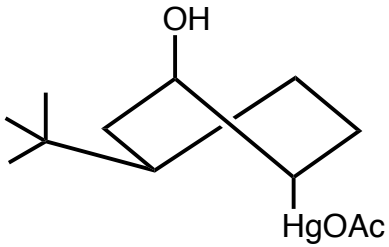


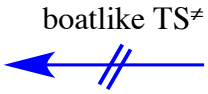


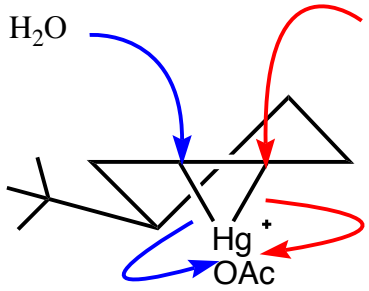


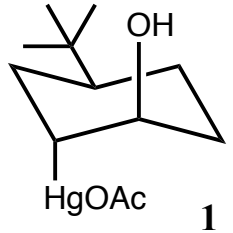
kinetically controlled; high energy TS's≠

kinetically controlled; low energy TS's≠

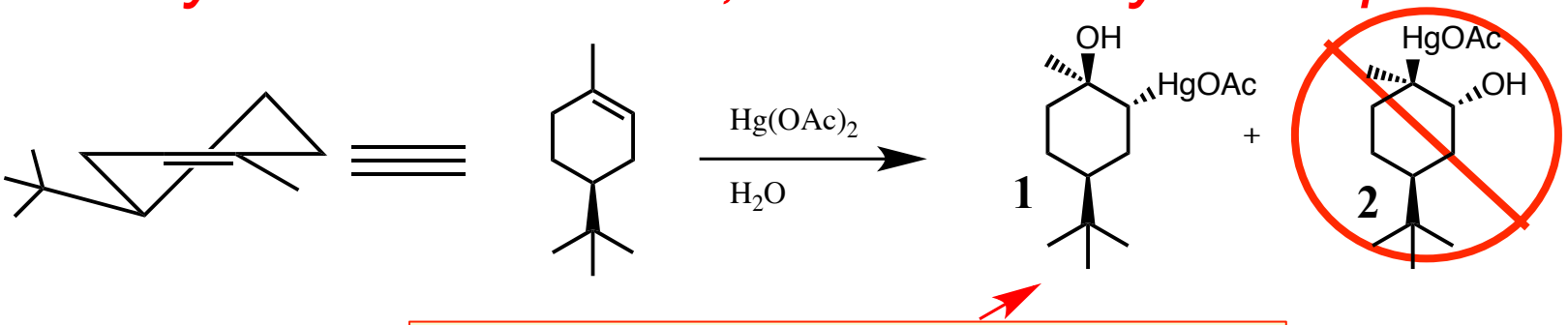






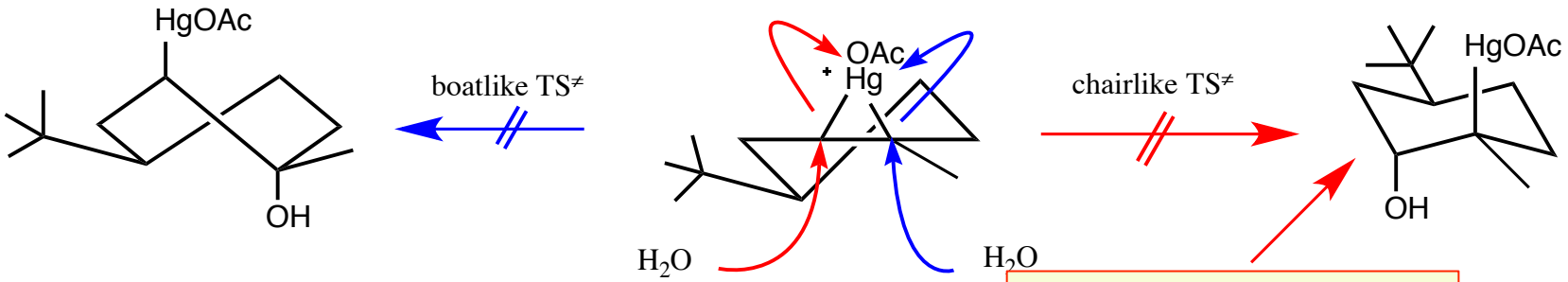


Oxymercuration – II; Add a Methyl Group



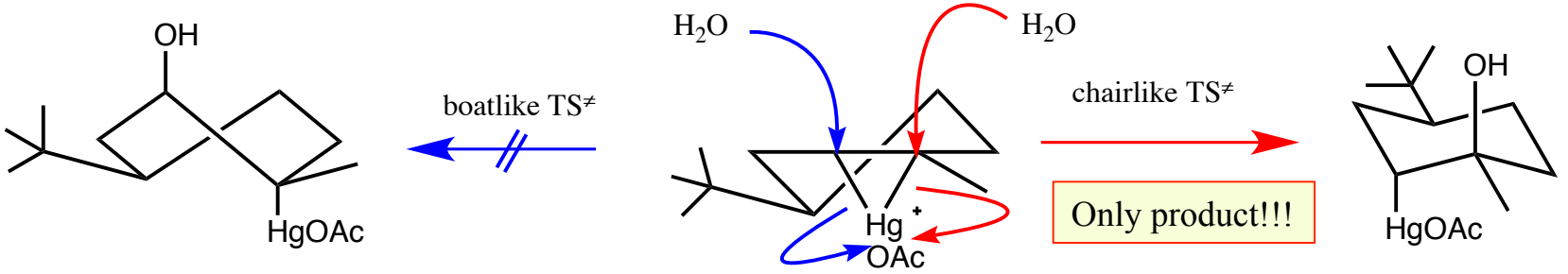
regiochemistry; anti addition; Markovnikov

regiochemistry; anti addition; anti - Markovnikov



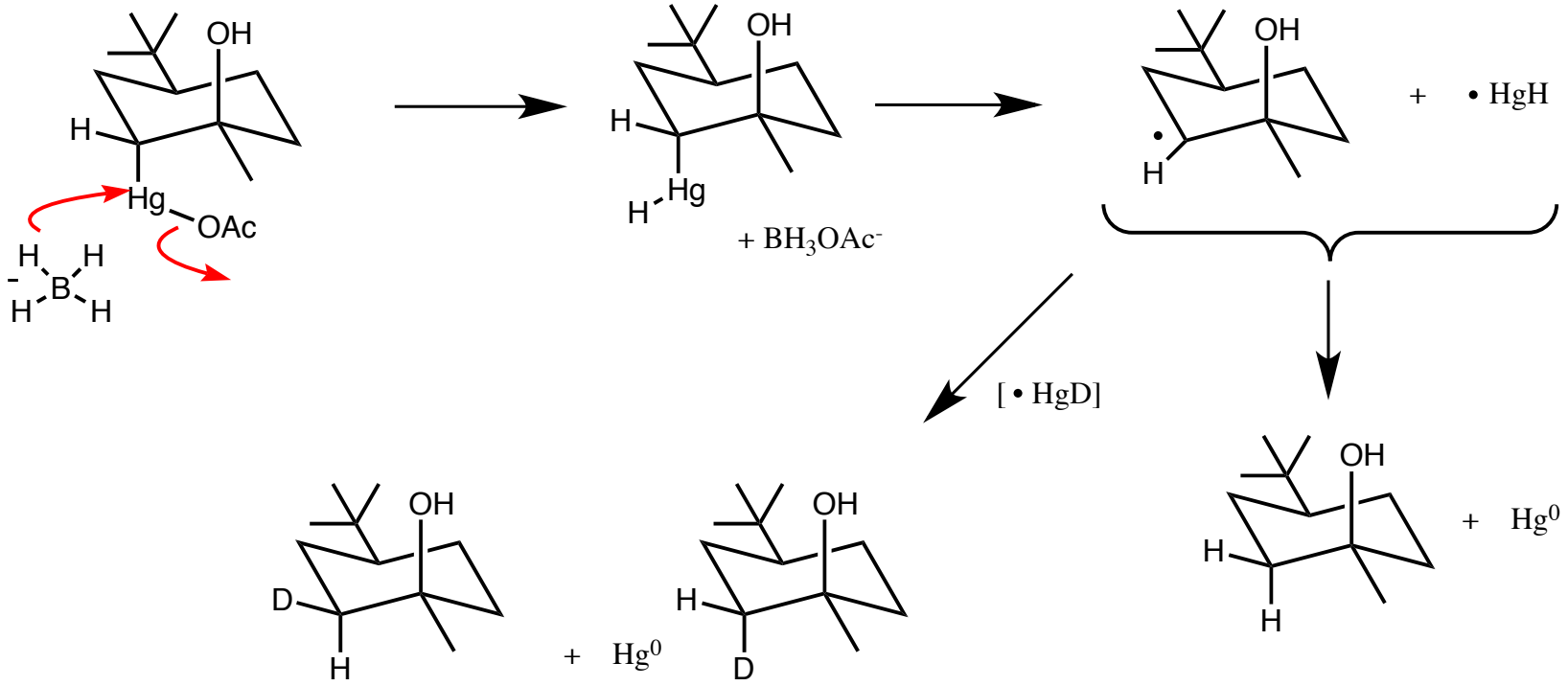
wrong regiochemistry

boatlike TS≠ eliminated on previous slide



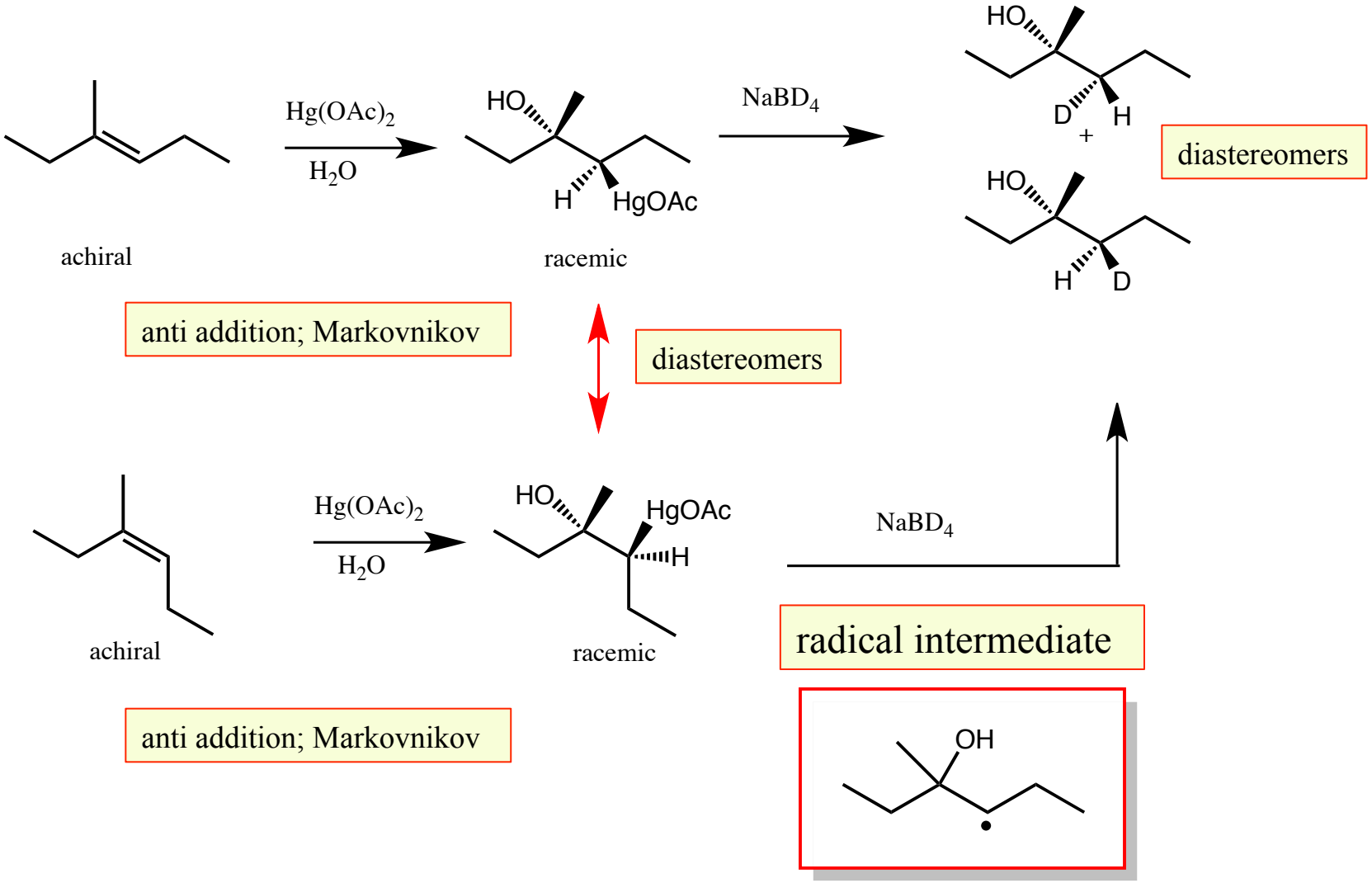
Only product!!!

Oxymercuration - III

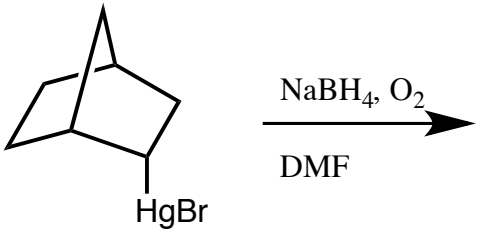


If BD_4^- had been used as the reductant, a mixture of deuterio compounds would form.

Oxymercuration - IV



Alkyl Mercurials – Radical Oxygenation

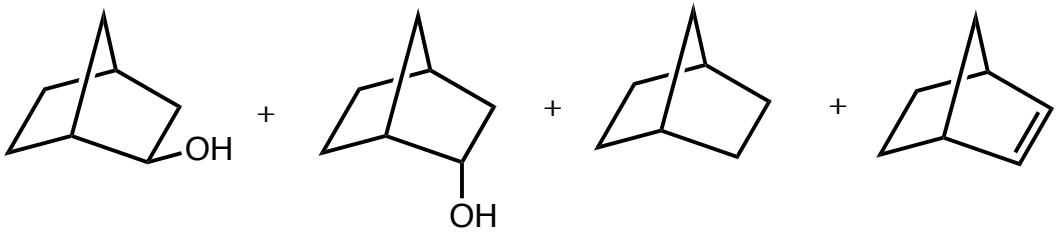


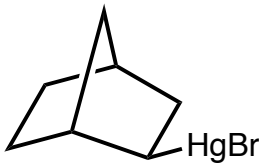
endo

$NaBH_4$, O_2

DMF

70% 17% 10% 1%



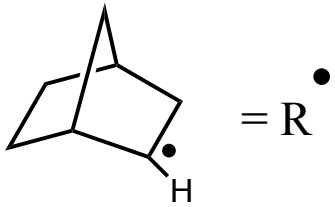


$NaBH_4$, O_2

DMF

73% 18% 11% 1%

exo



$= R^{\bullet}$

Endo and exo mercurials give the same radical.
Product distributions the same.

$RHgBr + BH_4^- \text{ --------> } RHgH$

$RHgH \text{ ---------> } R\cdot + \cdot HgH$

$R\cdot + O_2 \text{ ---------> } ROO\cdot$

$ROO\cdot + \cdot HgH \text{ -------> } ROOH + Hg^0$

$ROOH + BH_4^- \text{ --------> } ROH$

C. L. Hill and G. M. Whitesides,
J. Am. Chem. Soc., **96**, *1974*, 870.