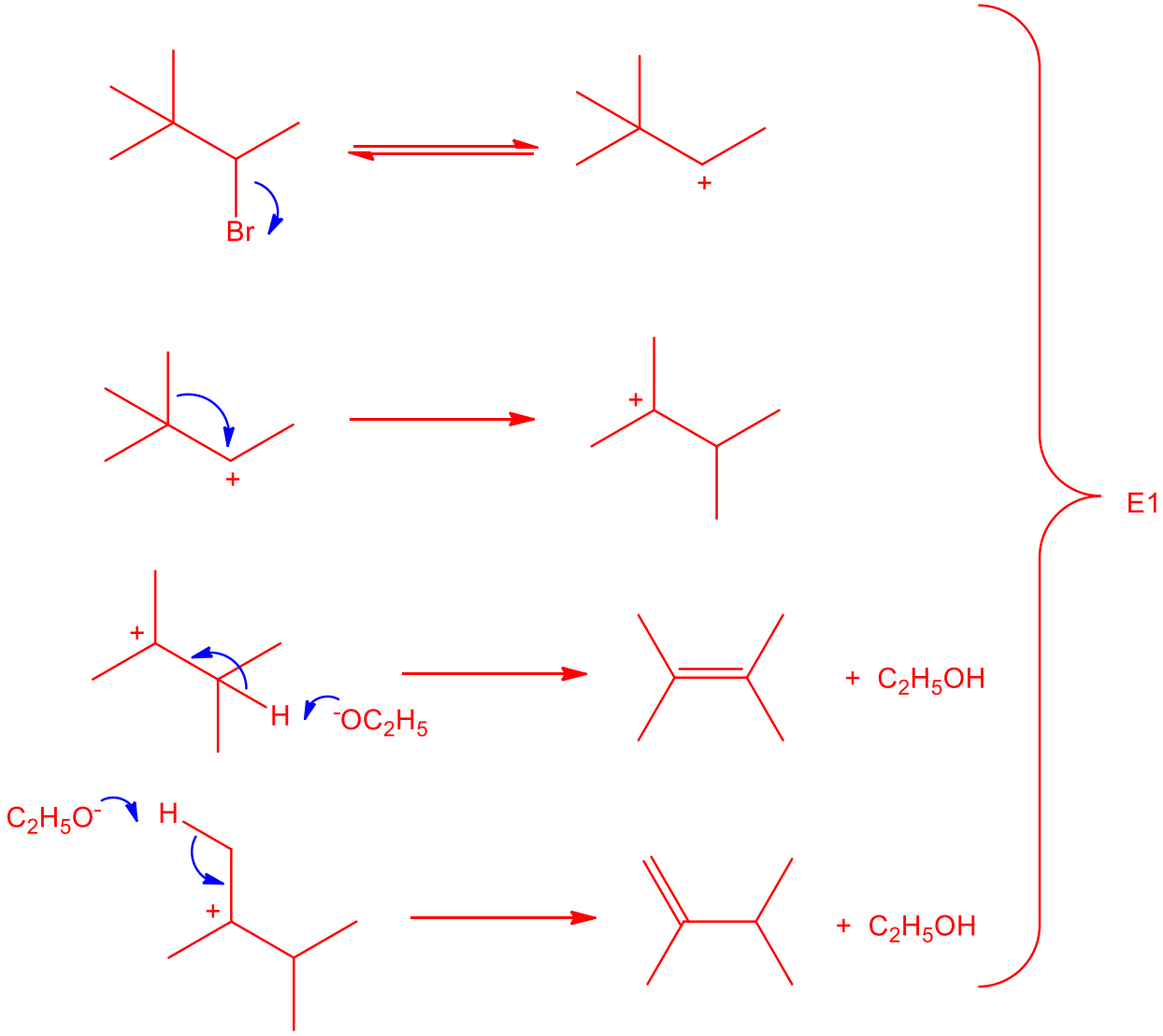
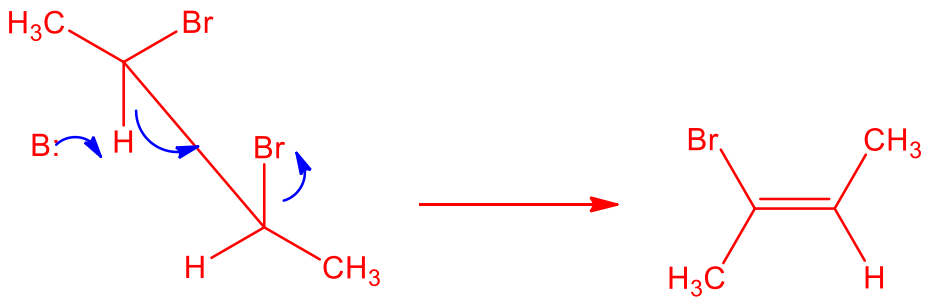
Exercise 13: - Elimination reactions

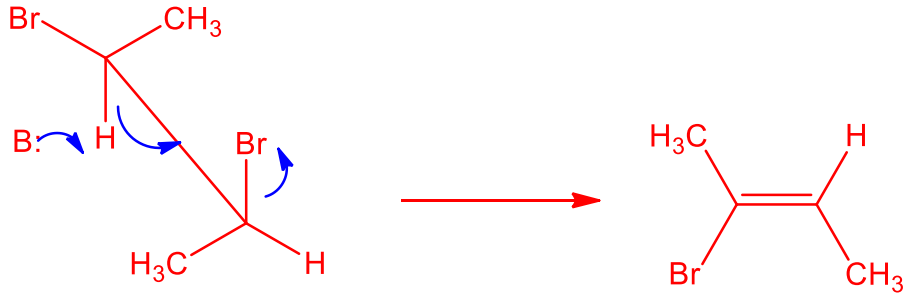
1. When 3-bromo-2,2-dimethylbutane is heated with a dilute solution of sodium ethoxide in ethanol, reaction follows first-order kinetics. Along with substitution, elimination occurs to yield 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene. Propose a mechanism for their formation.



2. Propose a mechanism for the formation of (*Z*)-2-bromo-2-butene from both (*R,R*) and (*S,S*)-2,3-dibromobutane via a dehydrobromination reaction.



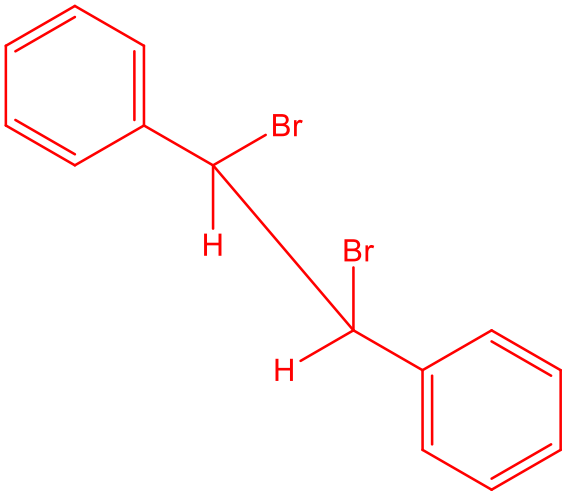
(2R,3R) (Z)



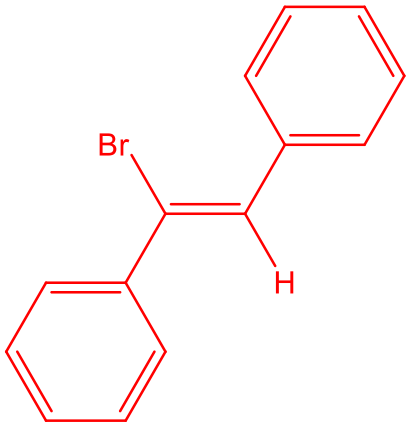
(2S,3S) (Z)

3. Partial dehydrohalogenation of (1R,2R)-1,2-dibromo-1,2-diphenylethane gives (Z)-1-bromo-1,2-diphenylethene.

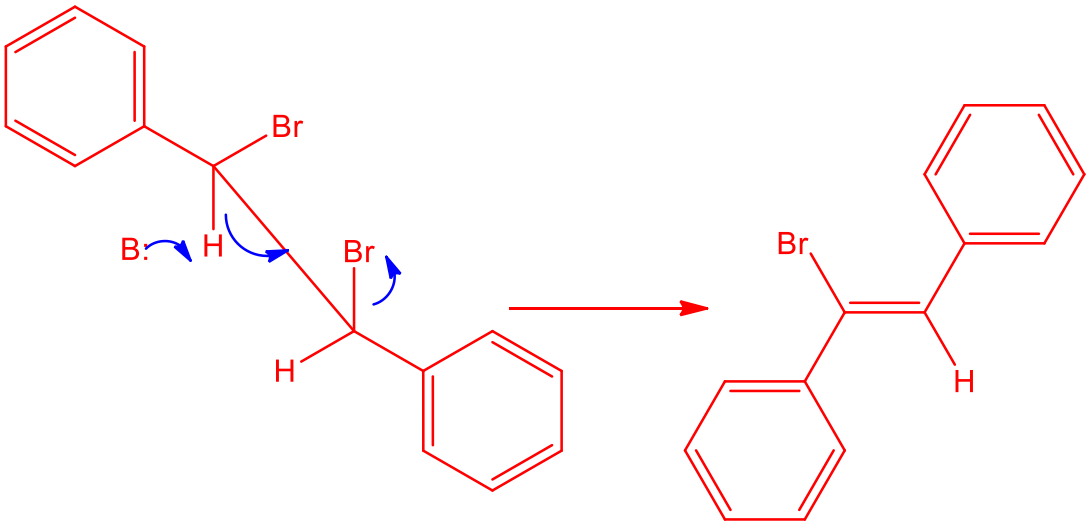
   a. Draw the structure of (1R,2R)-1,2-dibromo-1,2-diphenylethane.



   b. Draw the structure of (Z)-1-bromo-1,2-diphenylethene.

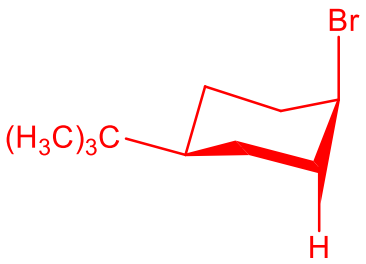


c. Propose a mechanism for this reaction.

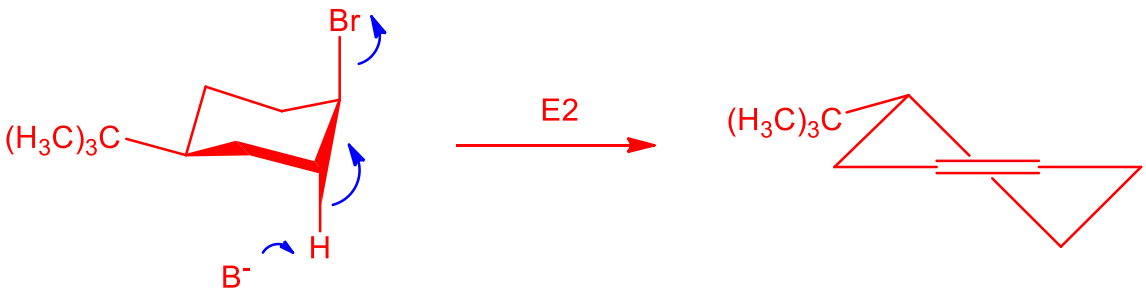


4. The rate of dehydrohalogenation of *cis*-1-bromo-4-*tert*-butylcyclohexane is proportional to the concentration of both the bromide and the base whereas the rate of dehydrohalogenation of the *trans* isomer is only proportional to the concentration of the bromide.

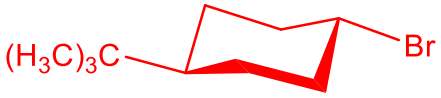
a. Draw the structure of *cis*-1-bromo-4-*tert*-butylcyclohexane.



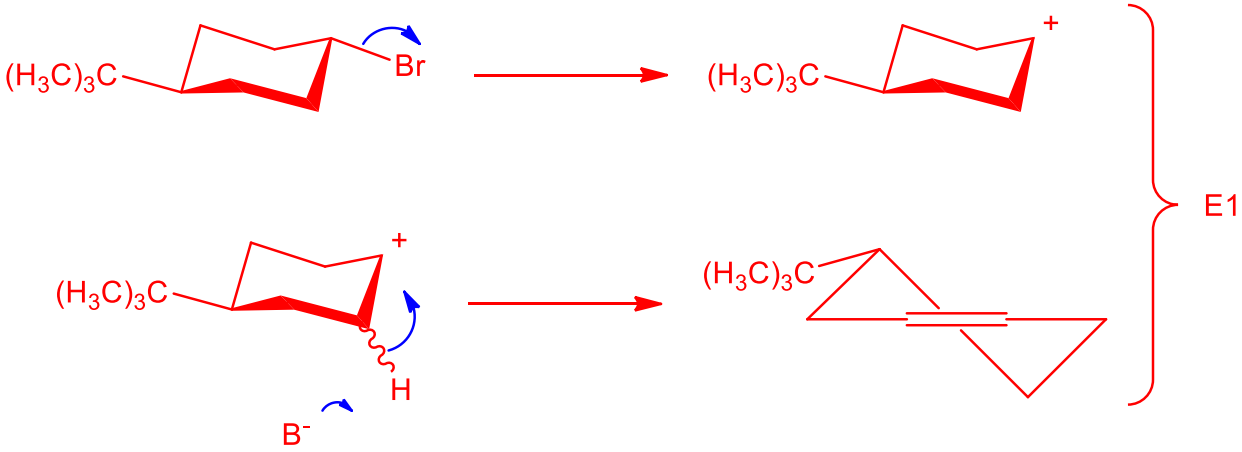
b. Propose a mechanism for the dehydrohalogenation of the *cis*-1-bromo-4-*tert*-butylcyclohexane.



c. Draw the structure of *trans*-1-bromo-4-*tert*-butylcyclohexane.



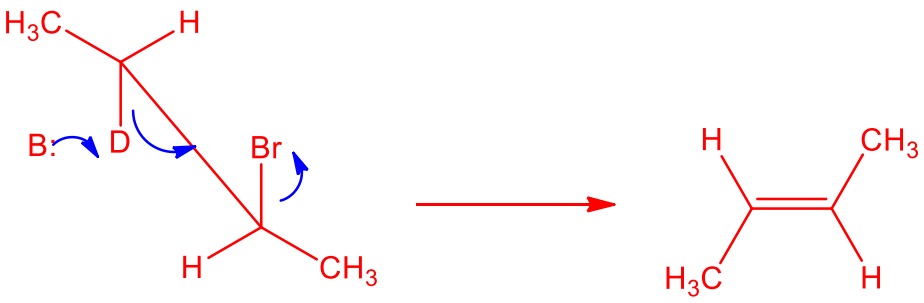
d. Propose a mechanism for the dehydrohalogenation of the *trans*-1-bromo-4-*tert*-butylcyclohexane.



e. Explain why the *trans*-1-bromo-4-*tert*-butylcyclohexane cannot react by a second order mechanism.

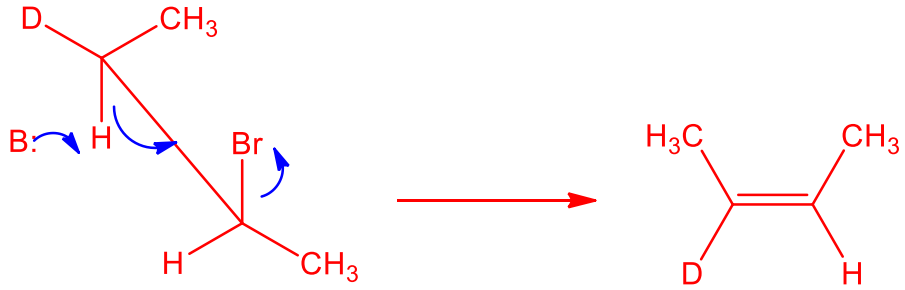
The bulky *tert*-butyl group has to be equatorial forcing the bromine into an equatorial position. The anti arrangement necessary for an E2 elimination is not possible.

5. Base treatment of (*2R,3S*)-2-bromo-3-deuteriobutane gave, in addition to the deuterated 1-butene, only (*Z*)-2-deuterio-2-butene and (*E*)-2-butene. Explain.



(2R,3S)

(E)



(2R,3S)

(Z)