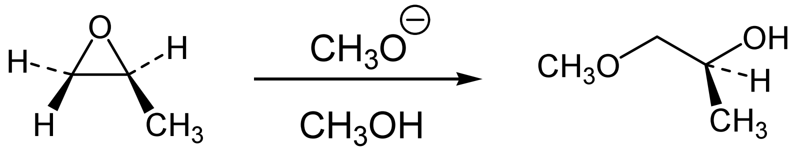
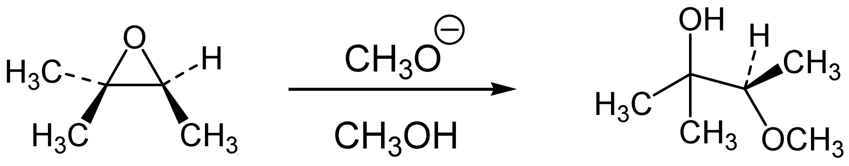
Opening of Epoxides

Direct Nucleophilic Ring-Opening

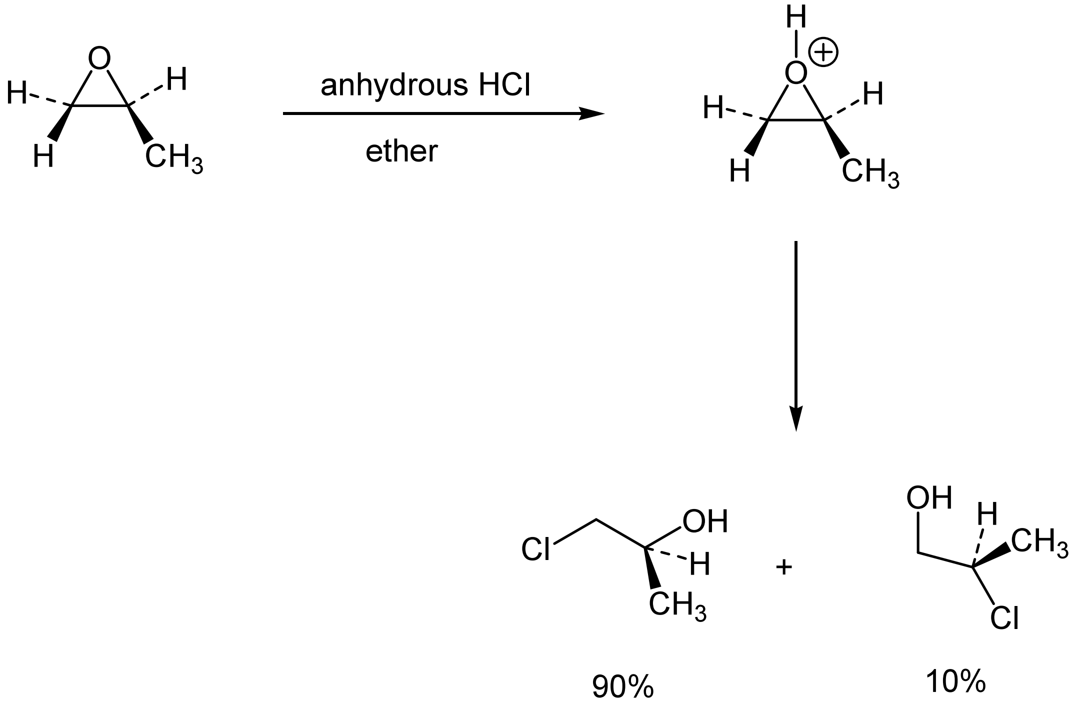
The regiochemistry of ring-opening is determined by the relative rates for S_N2 reactions – i.e. primary > secondary and no reaction at tertiary. For example:

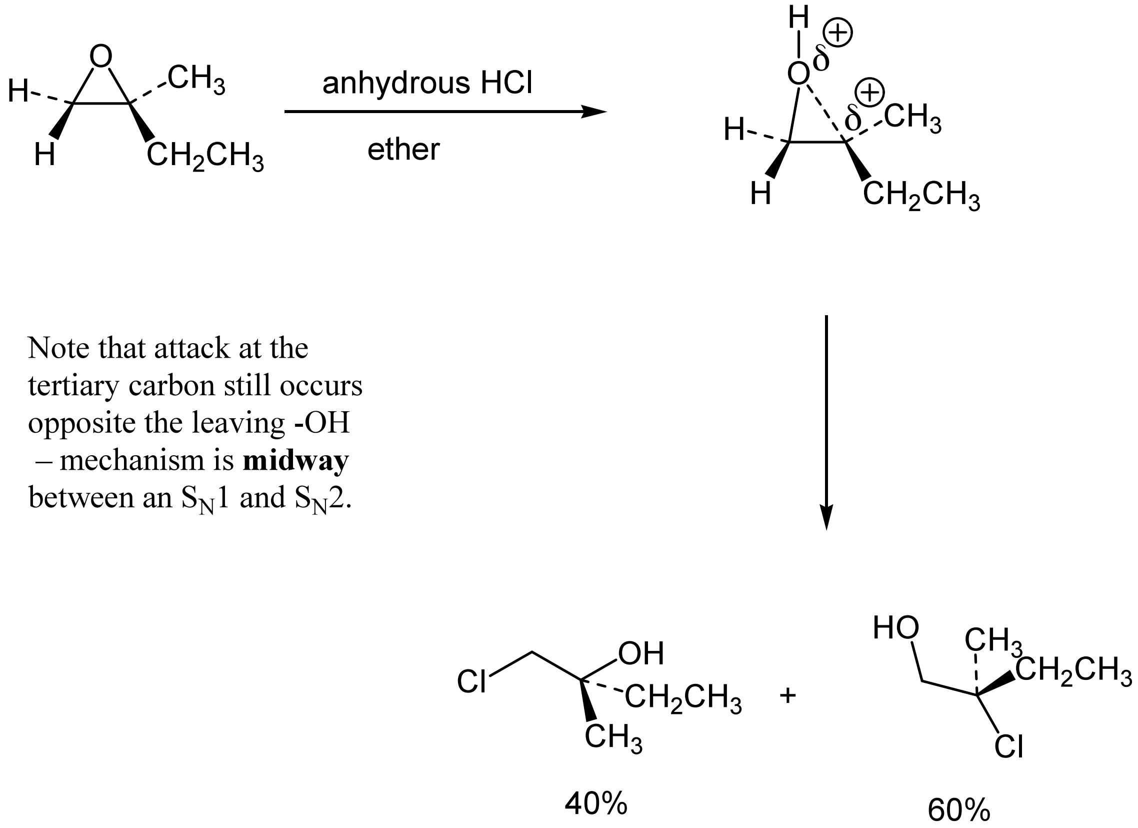




Acid Catalysed Ring-Opening

The regiochemistry of ring opening is more complicated: primary reacts faster than secondary for steric reasons, but tertiary reacts faster than secondary or primary for electronic reasons.

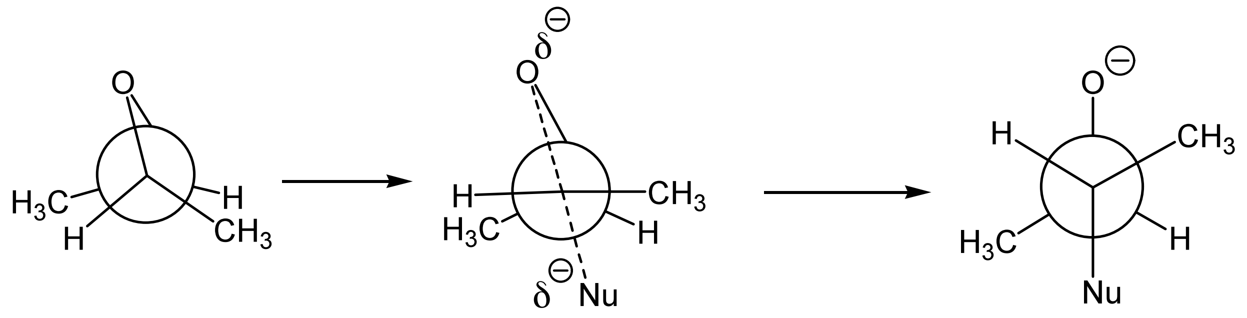


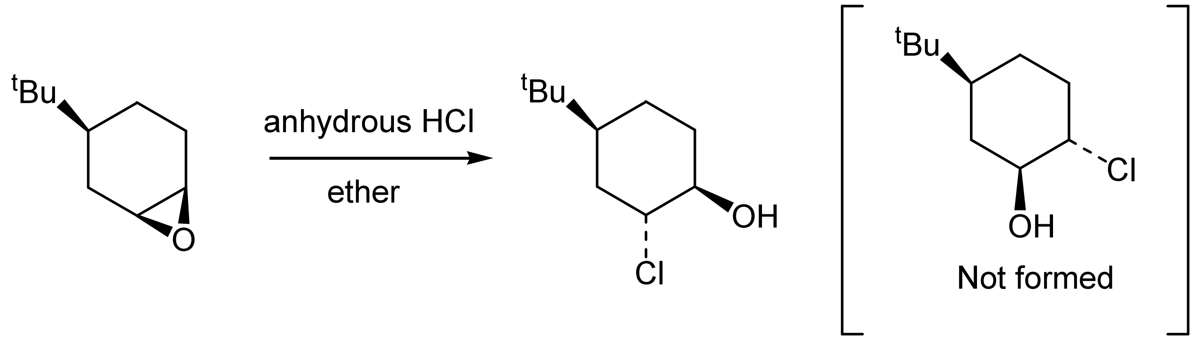


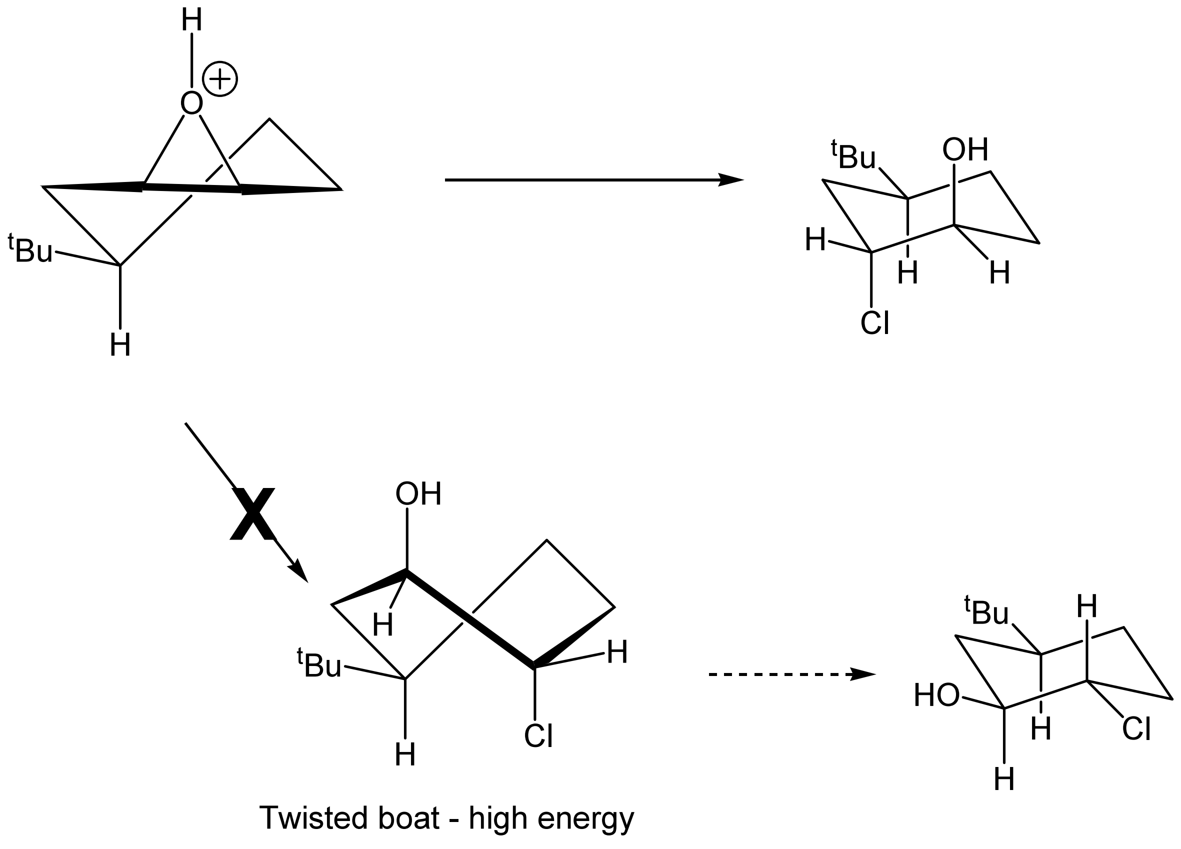
Note that attack at the tertiary carbon still occurs opposite the leaving -OH – mechanism is **midway** between an S_N1 and S_N2.

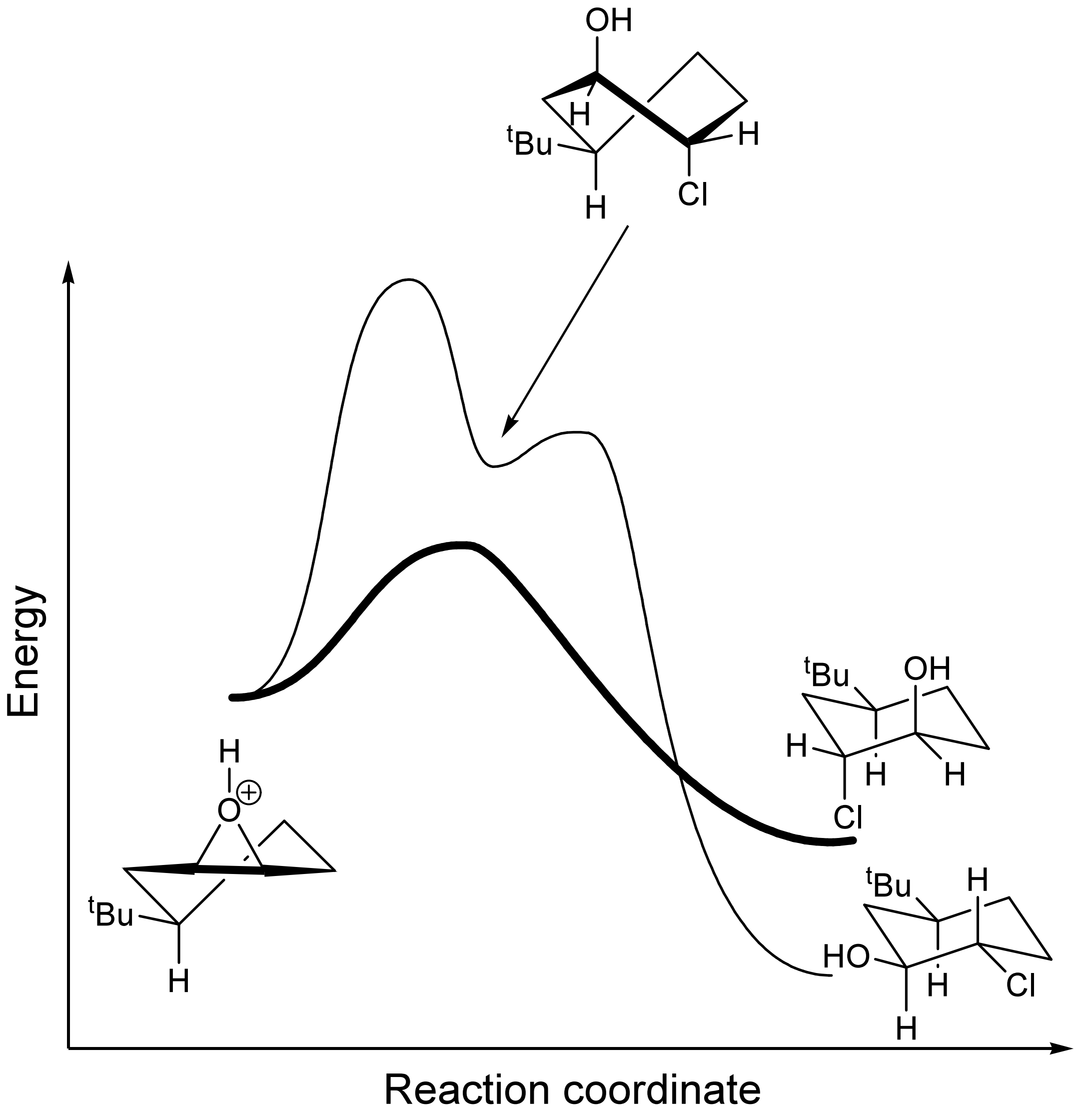
Regiochemistry for Cyclic Systems

The mechanism of ring opening requires that the leaving -$O^{\ominus}$ or -OH group be *anti* and at 180° to each other. In cyclic systems ring opening occurs to give **trans-diaxial** products.








OH
H
^{t}Bu
H
H
Cl
Energy
H
O
^{t}Bu
H
^{t}Bu
OH
H
H
H
Cl
^{t}Bu
H
HO
H
Cl
H
Reaction coordinate