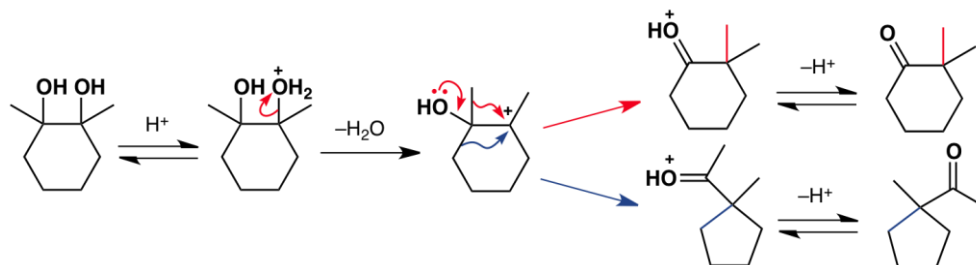
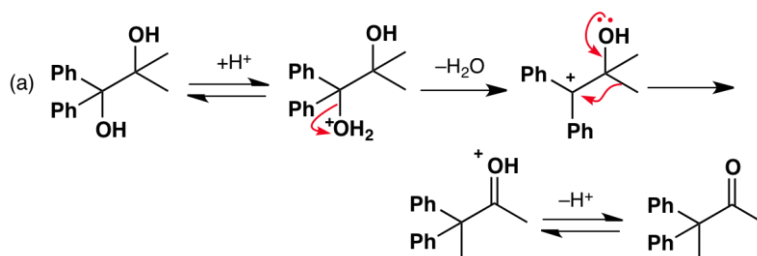


Solutions to Exercises, Chapter 22

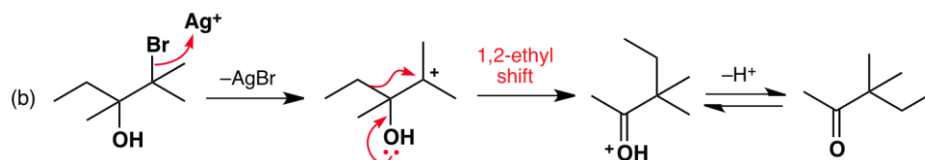
22.1



22.2

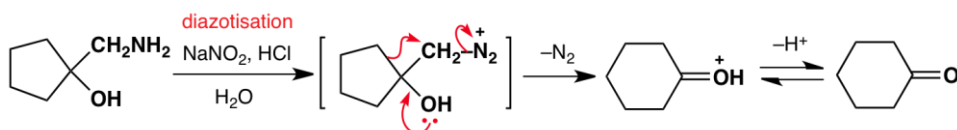


The more stable phenyl-conjugated carbenium ion is formed in the first step.



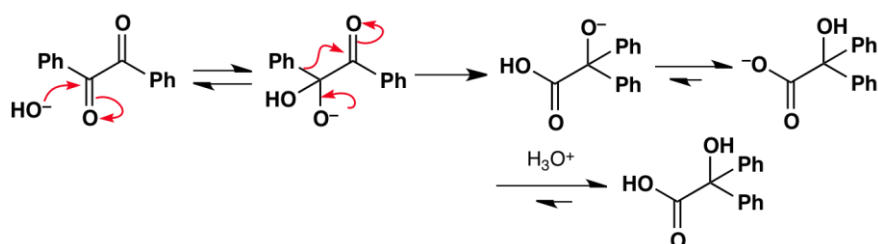
The ethyl group has a higher migratory aptitude than the methyl in this semi-pinacol rearrangement.

22.3

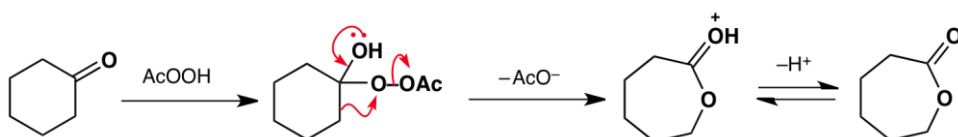


This is an example of a semi-pinacol rearrangement.

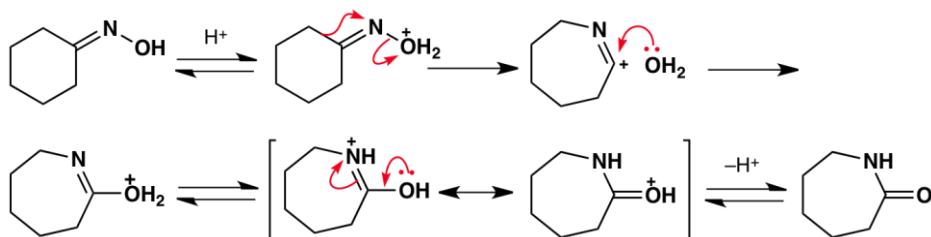
22.4



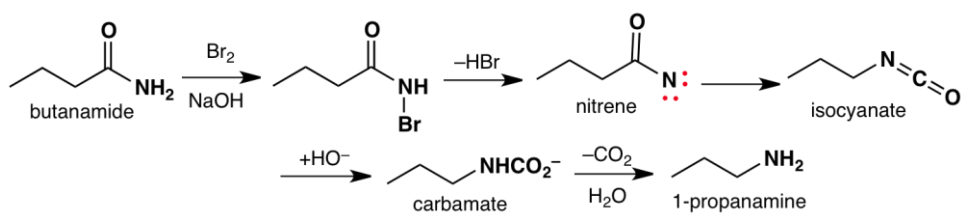
22.5



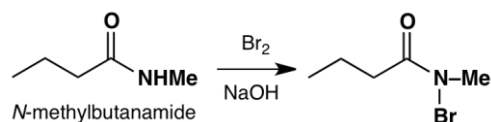
22.6



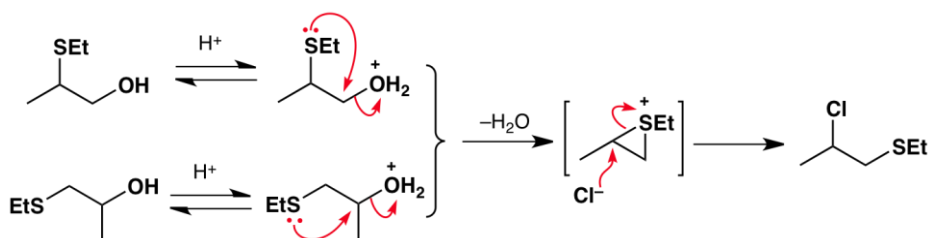
22.7



The N -bromo product of N -methylbutanamide cannot undergo an α -elimination to give the nitrene so the reaction goes no further than the N -bromoamide.



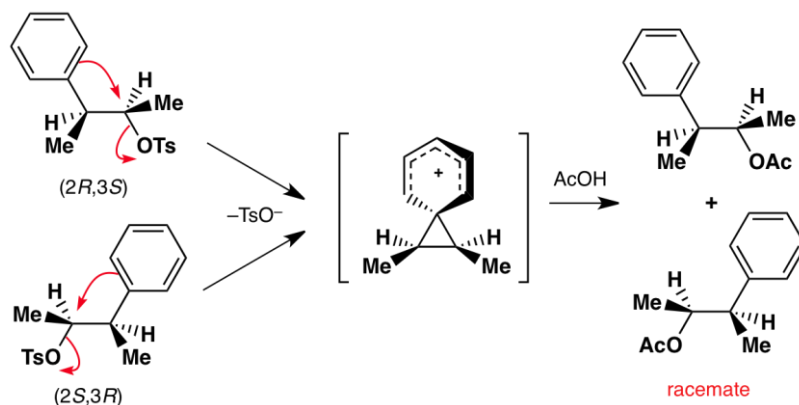
22.8



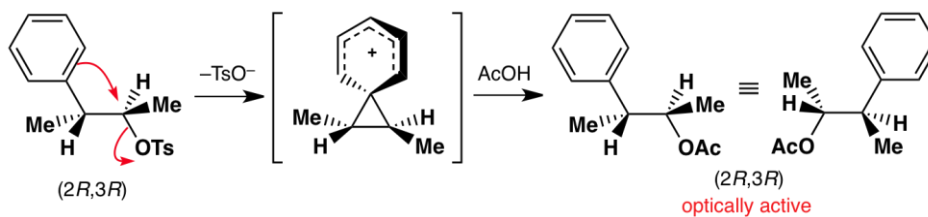
The both isomers give the same cyclic sulfonium ion and the attack of chloride at this intermediate occurs regioselectively at the carbon with the higher positive charge even though it is the more substituted.

22.9

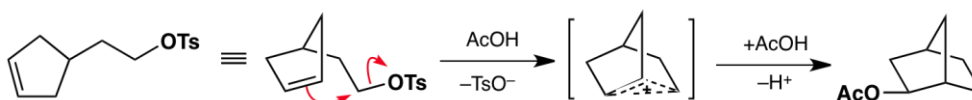
(a)



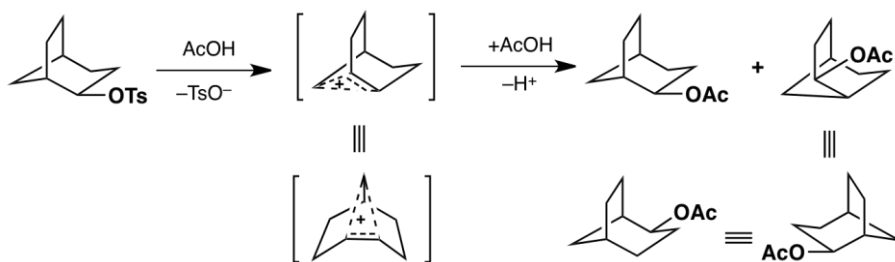
(b)



22.10 The alkene acts as a neighbouring group to displace the tosylate nucleofuge and form the same (symmetrical) norbornyl cation we encountered in Scheme 22.14.



22.11



The symmetry of the intermediate cation requires that its nucleophilic capture will lead to racemic product.