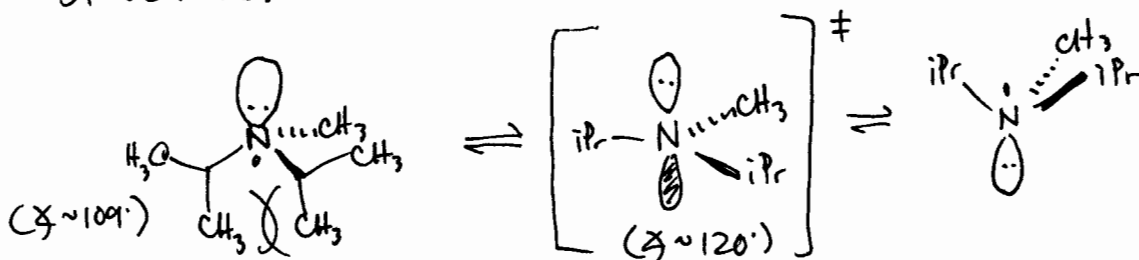
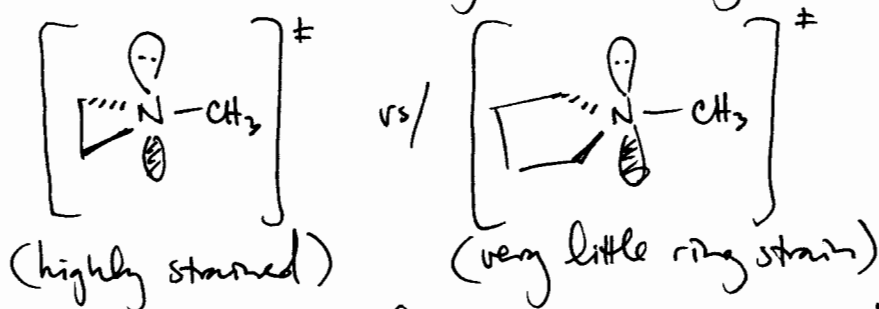


Problem Set 4 Answer Key

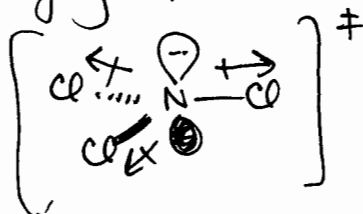
1. a) The barrier to inversion for iPr_2NMe is less than for Me_3N because going from sp^3 (tetrahedral) to sp^2 (trigonal planar) spreads the bulky isopropyl groups further apart and relieves steric strain. In other words, the isopropyl groups destabilize the pyramidal amine more than the planar transition structure.



b) The sp^2 transition state has ideal bond angles of $\sim 120^\circ$. The aziridine TS is highly strained because it cannot achieve 120° due to the small ring locking the angles at $\sim 60^\circ$. The 5-membered ring can easily adopt 120° angles.

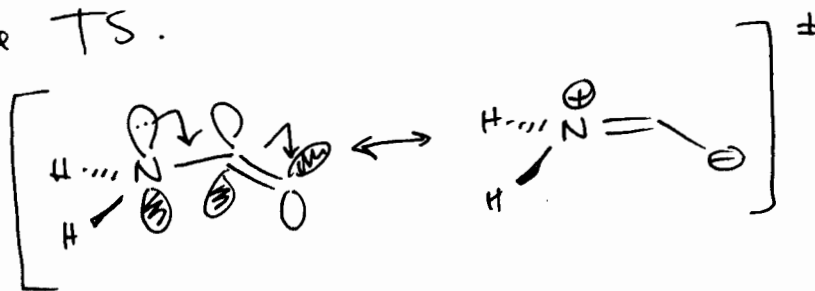


c) As the nitrogen goes from $sp^3 \rightarrow sp^2$, it becomes effectively more electronegative. (Remember: more s-character means more electronegative) The electronegative chlorine atoms pull electron density away from N more than the methyl groups, creating an electron-deficient N, and destabilizing the TS.

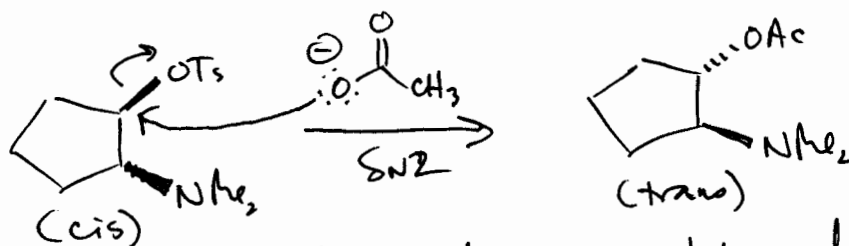


Problem Set 4 Answer Key

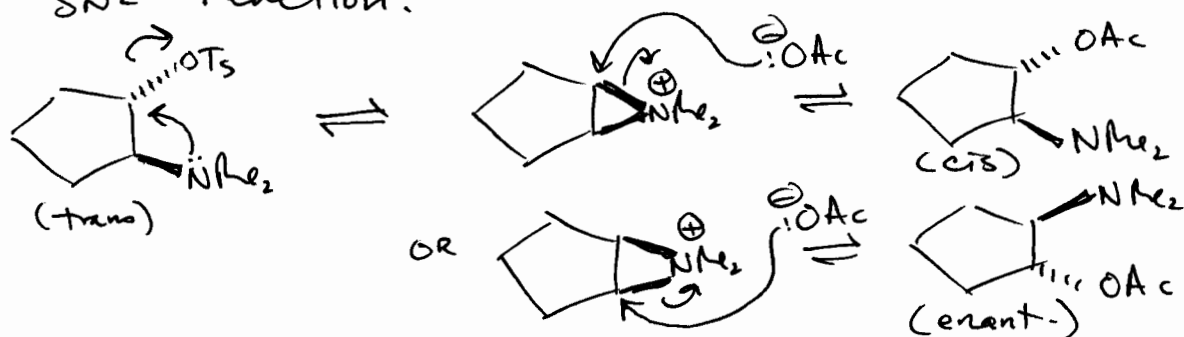
1. d) The barrier to inversion for vinylamine is less than for ammonia because the TS is stabilized by orbital overlap between the filled p-orbital on N and the π^* of the alkene. Delocalization of the lone pair stabilizes the TS.



2.

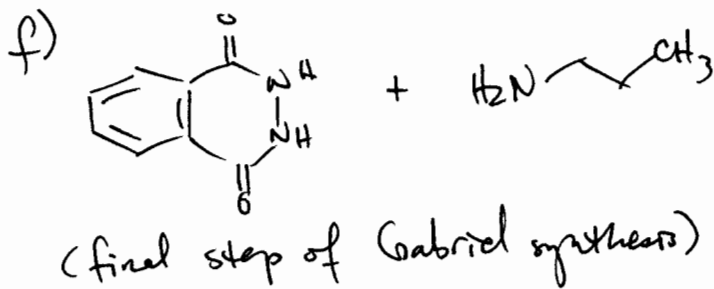
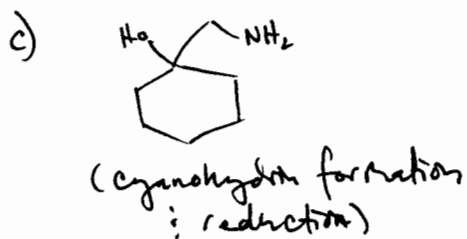
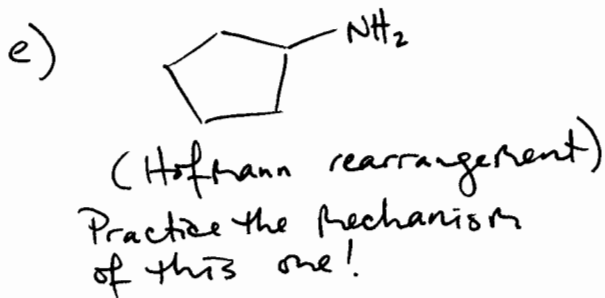
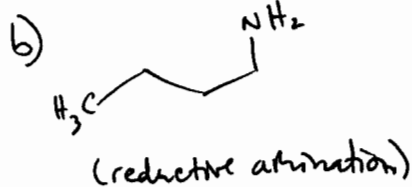
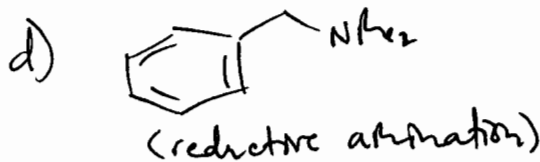
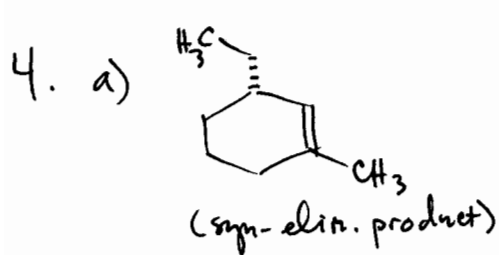
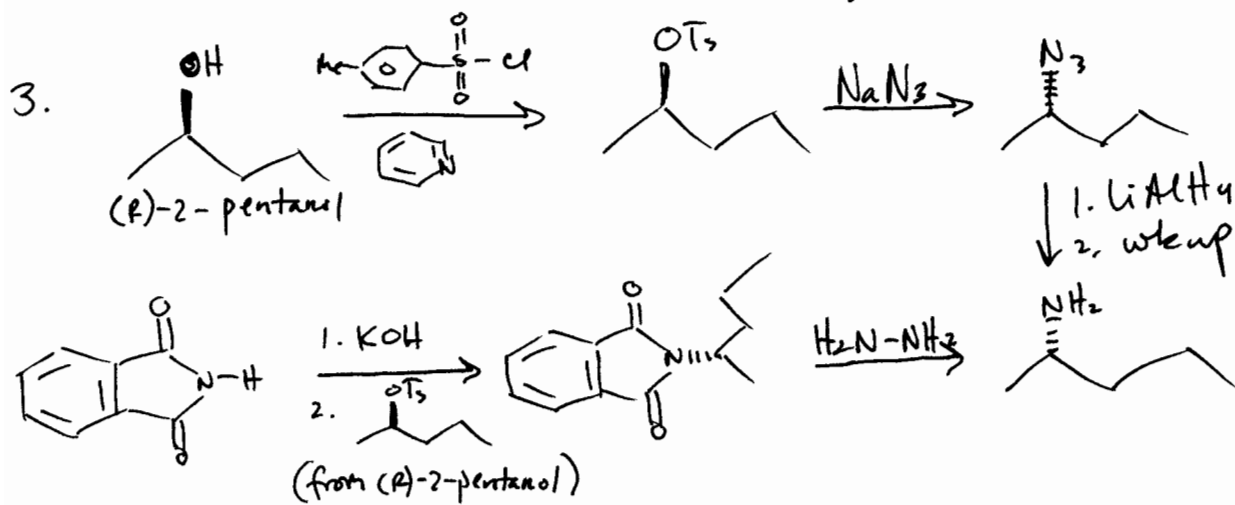


The trans (inverted) product is obtained through an S_N2 reaction.



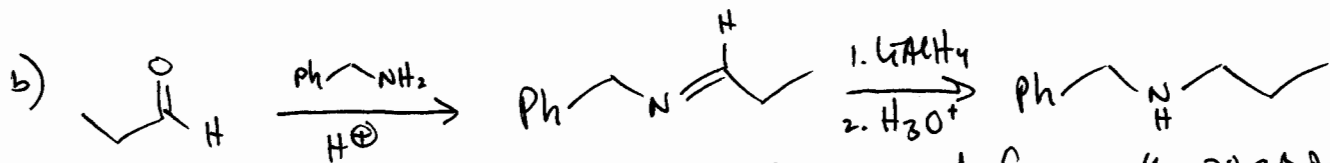
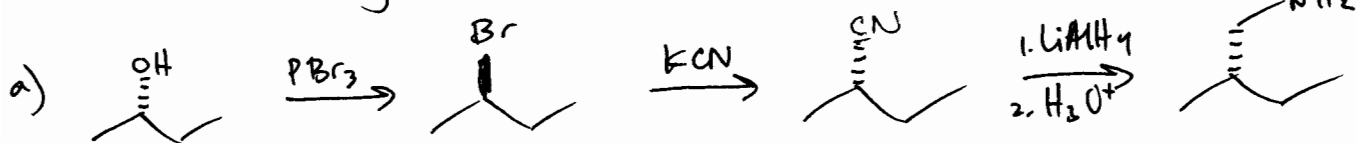
In the trans isomer, displacement of the tosylate to form the aziridine is faster than S_N2 . Both enantiomers of the cis-product are formed because the aziridine intermediate is achiral. The acetate nucleophile can attack at either carbon.

Problem Set 4 Answer Key



Problem Set 4 Answer Key

5. There may be other ways to make these molecules!



Remember: One-step reductive amination would form the 3° amine!

