

Problem Set 2

Templates

2.1 Problem 2

9/25: • We now begin discussing Problem 2.

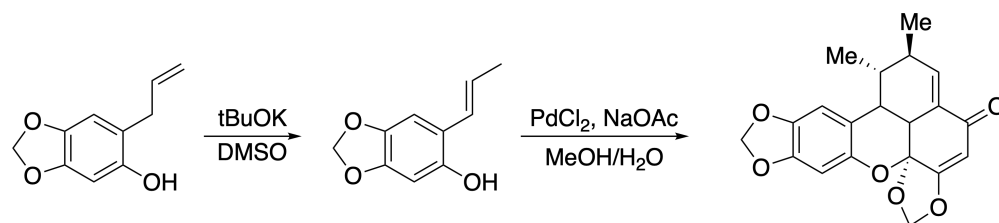


Figure 2.1: Wendlandt PSet 2, Q2.

- This is similar to an **Overman rearrangement**.
- Palladium is unlikely to activate the aromatic π -system — and if it did, it would do so in an η^6 -fashion. There are better things for it to coordinate to.
- A Wacker oxidation is net oxidative, whereas this is a redox neutral reaction.
- Palladium is proposed to be a **template** in this reaction; that is, it is to bring the fragments together.
- Frank's proposal is much closer.
 - He sees the “latent *ortho*-quinone methide.”
 - Entry into the dimerization steps is by bringing the carbon-carbon backbone together.
- In solution, PdCl_2 will get solvated immediately to have two X-type ligands and two L-type ligands, so that part of my proposal was correct.
 - $\text{PdCl}_2(\text{MeOH})_2$ could then ligand exchange with the substrate, which also has a good L-type ligand and X-type ligand.
 - Kicking out HCl 's will lead to NaCl and HOAc in basic solution.
- Think about the π -orbitals on the alkene L-ligand that would interact with palladium's d -orbitals.
- Alkenes really want to be perpendicular to palladium; crystal structures support this.
- Altogether, the full solution to PSet 2, Q2 is on the next page.

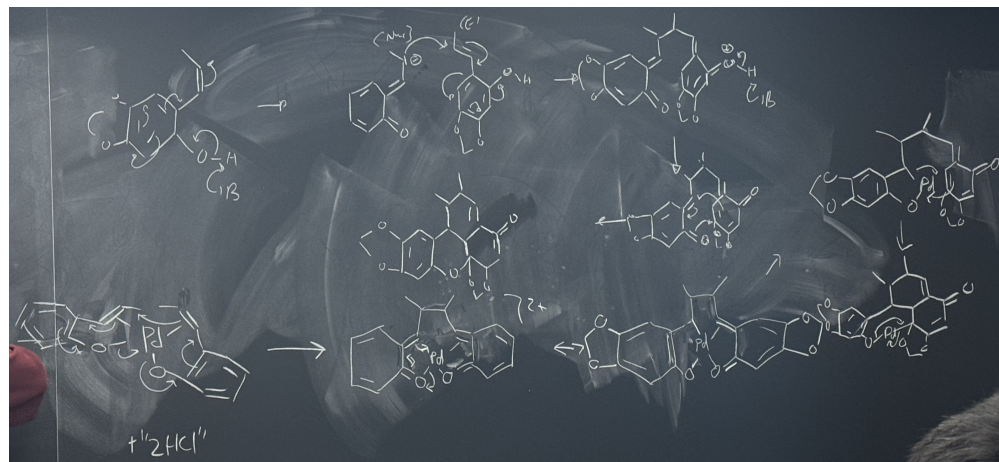


Figure 2.2: Wendlandt PSet 2, Q2 solution.