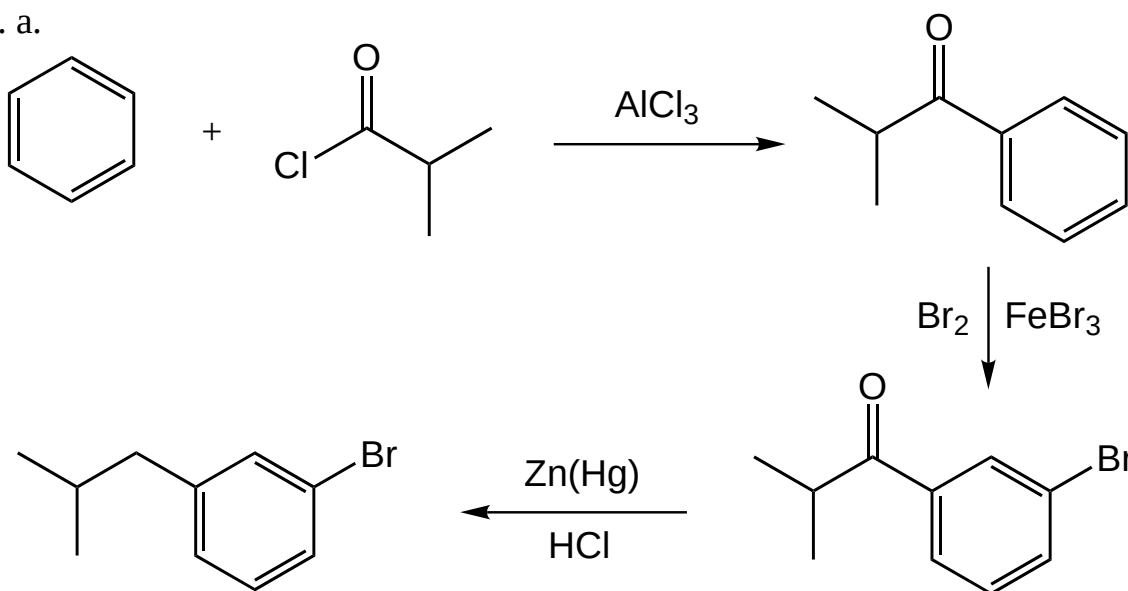


Organic Chemistry c3444y

Problem Set 3 - Answer Key

1. a.

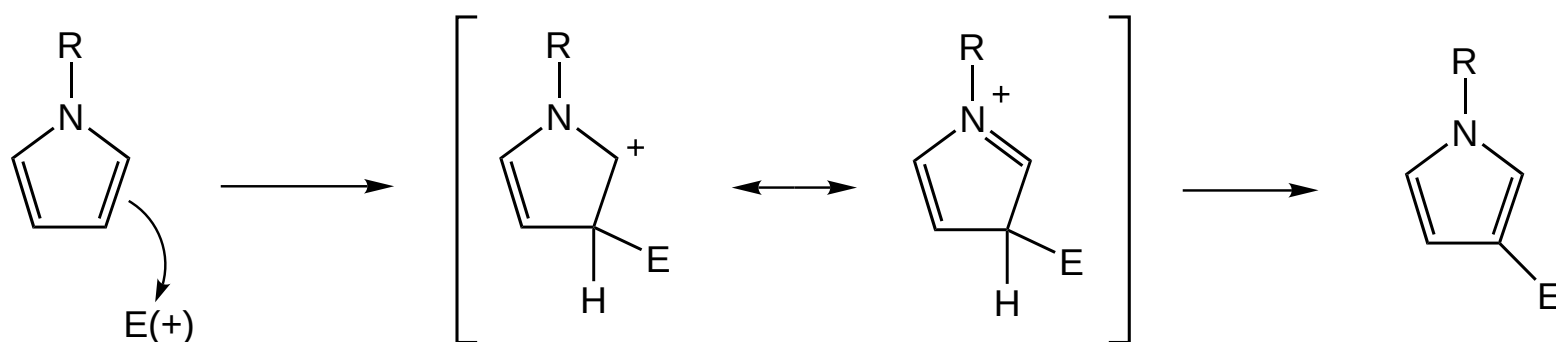
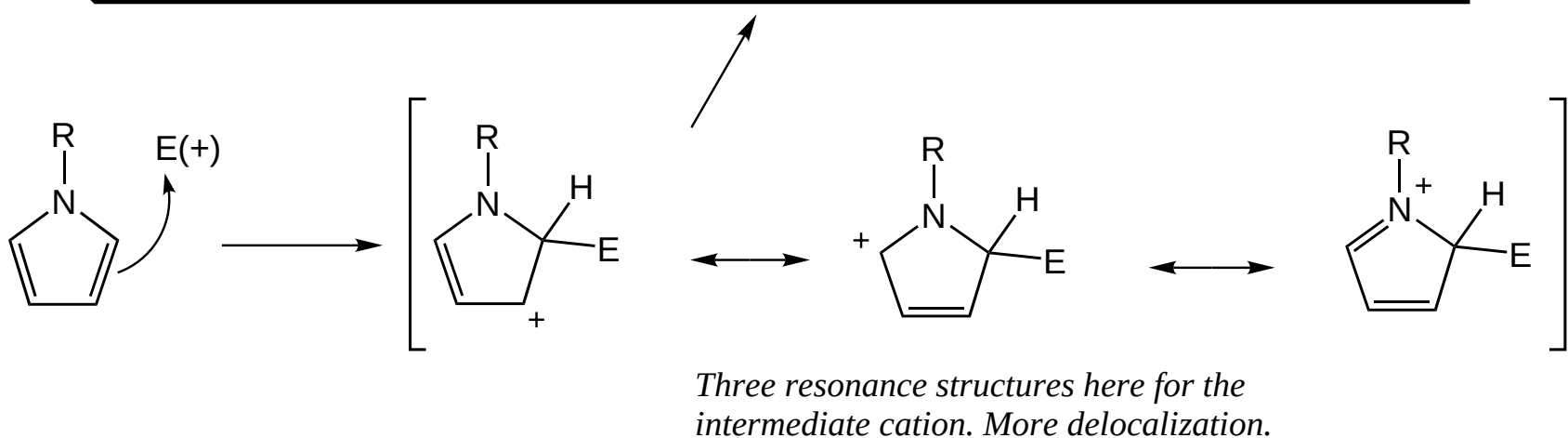
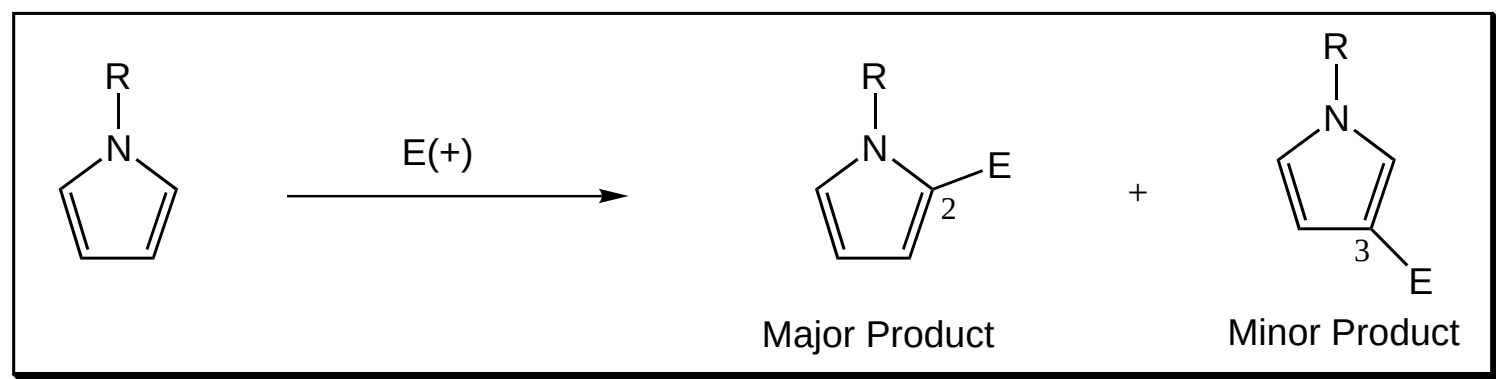


Analysis of the problem:

The target system has two ortho/para directors. There can be no two step synthesis, therefore. We also cannot put an iso-butyl group on directly. So we need a meta director that can be turned into an iso-butyl group.

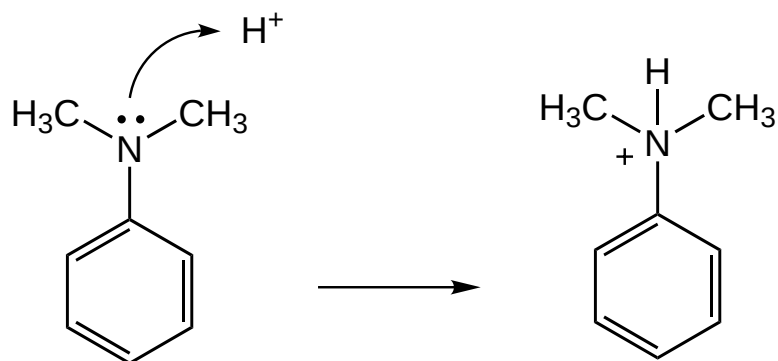
b. Same idea as 14.33 c in the book, see the study guide.

2.



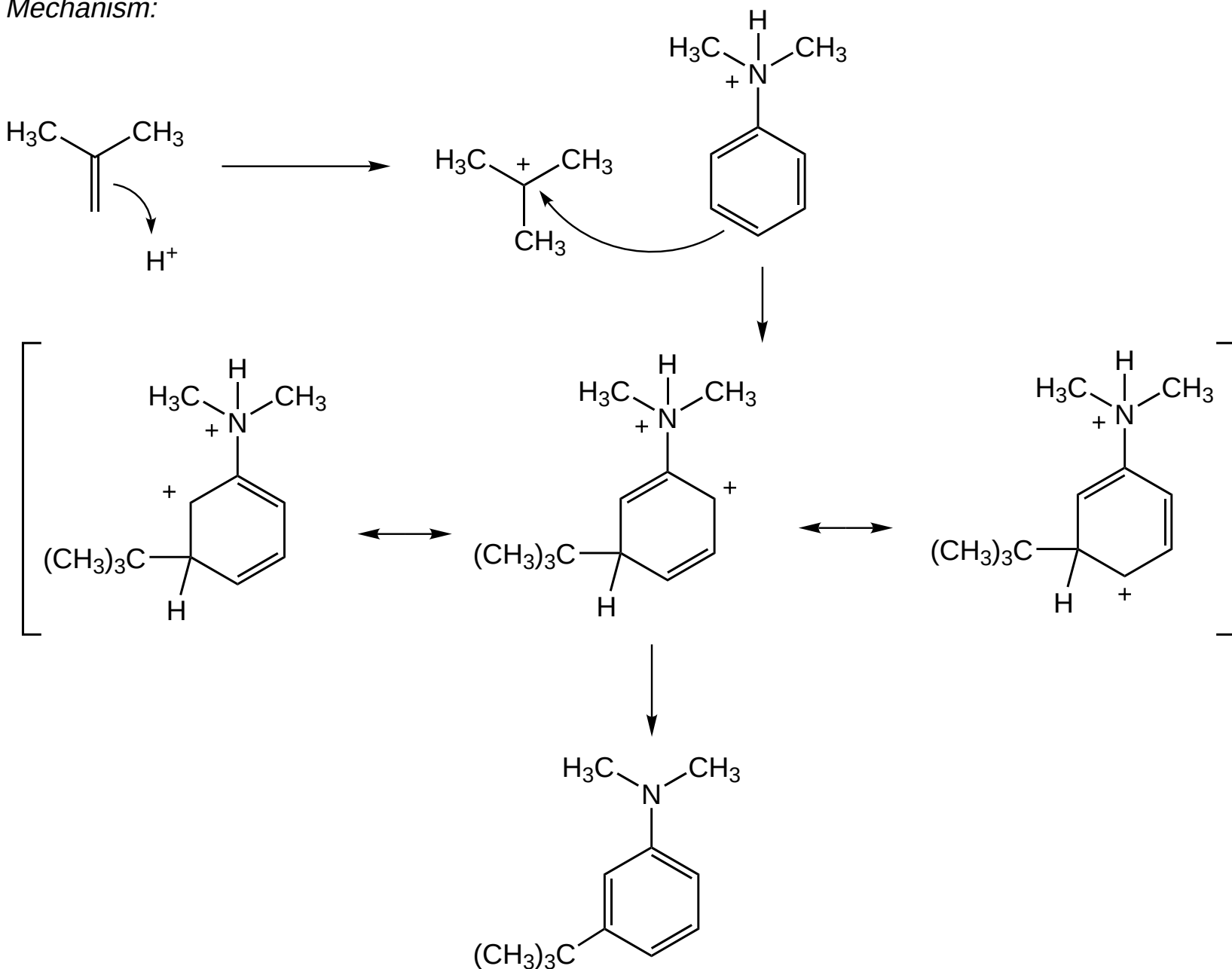
Only two resonance structures here for the intermediate cation. Less delocalization.

3. The nitrogen of *N,N*-dimethylaniline is a basic nitrogen! Yes, the nitrogen is sp^2 and the lone pair is involved in resonance, but it is not directly involved in the aromaticity. Therefore, it is still basic, albeit weakly. But sulfuric acid is a very strong acid, so what will be the very first thing that will happen:

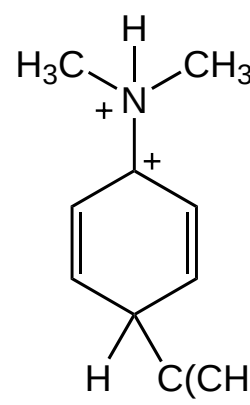


Now, because of the positive charge, and the lack of a lone pair, this group is a deactivator and a meta director!

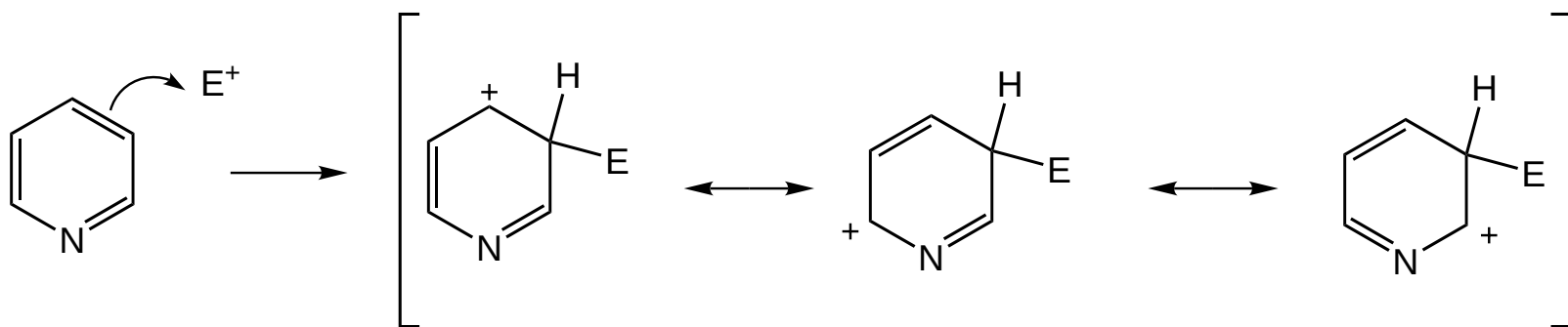
Mechanism:



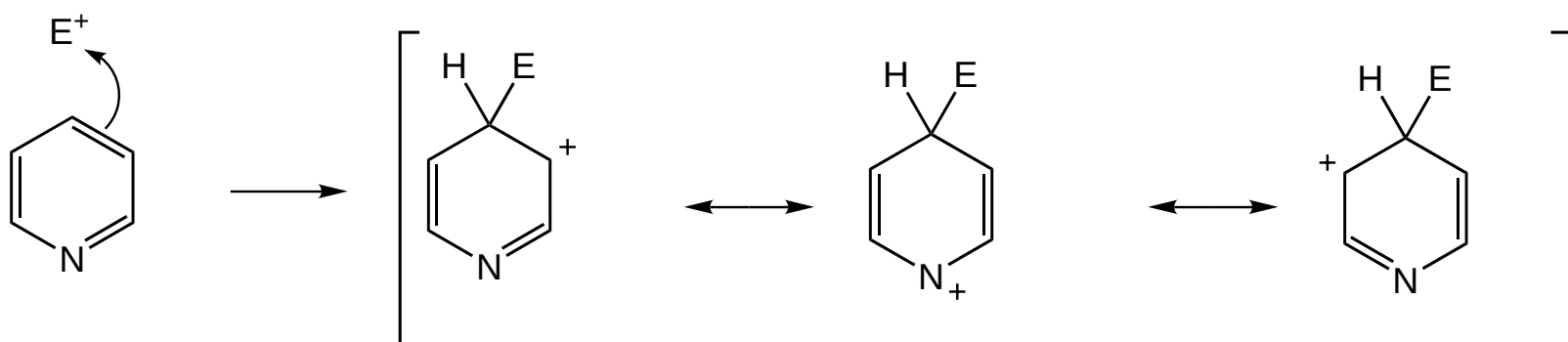
Recall that para (or ortho) attack would involve the following very poor contributor:



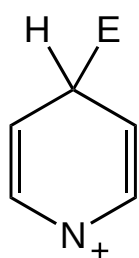
4. a. Draw the resonance structures for the intermediate arenium ion formed from attack at the 3 position:



b. Draw the resonance structures for the intermediate arenium ion formed from attack at the 2 (or 4) position:



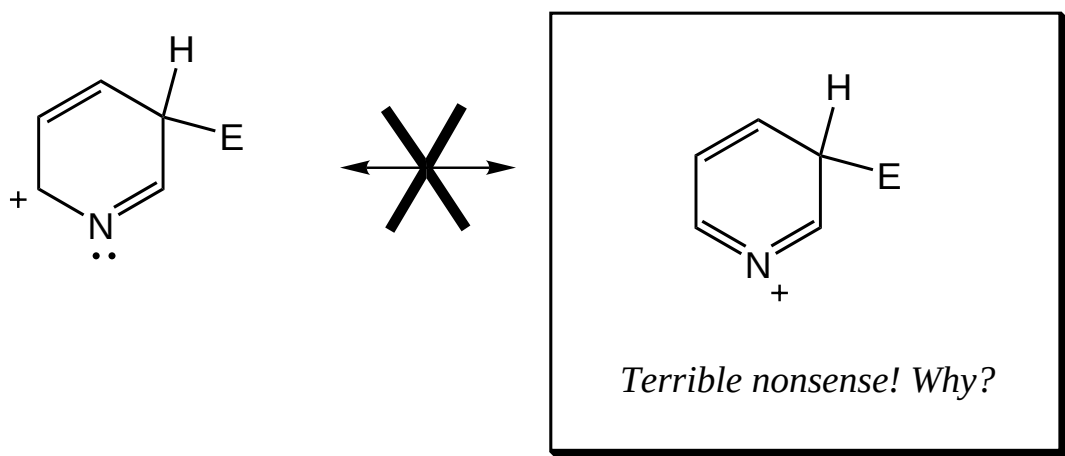
c. What is it that makes attack at the 2 (or 4) position especially slow relative to attack at the 3 position?



Three resonance structures for both, but this one is an especially poor contributor. Positive charge on relatively electronegative nitrogen.

(Do not confuse with the resonance structures for problem 2, where a positive charge on N is acceptable, because there is still a full octet. Above, the N is suffering with only 6 electrons.)

NOTE: The following is an INVALID resonance structure:



If you did this in your answer to part a, make sure you understand why you shouldn't have.