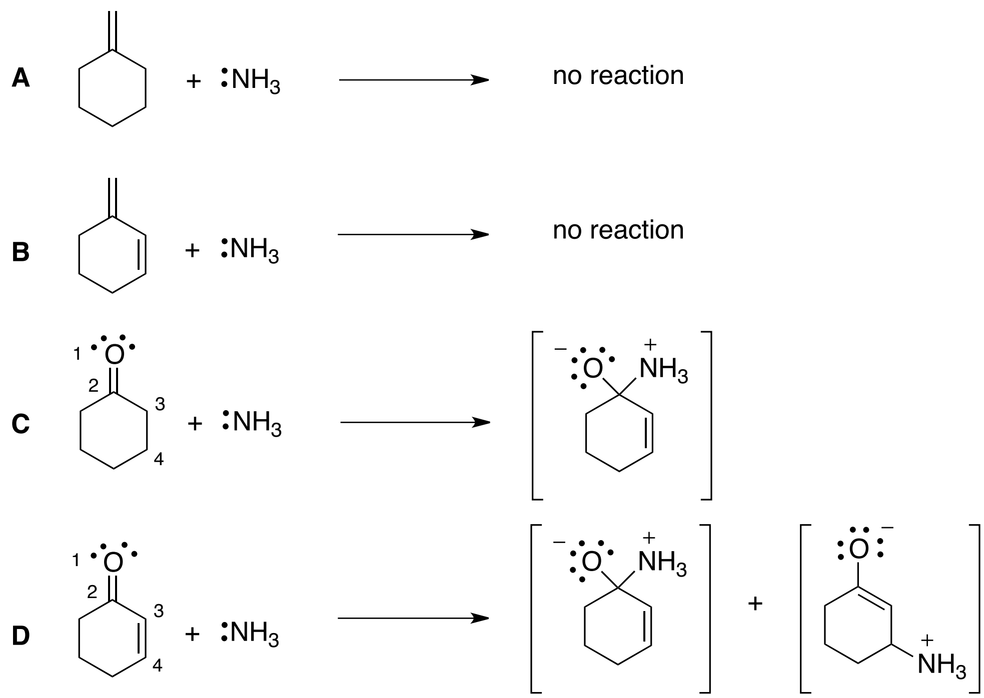
CHAPTER 2: RESONANCE THEORY (cont.)

Example 2.

When ammonia is added to the hydrocarbons shown in **A** and **B**, no reactions occur. When an oxygen is added to the structure at position 1, ammonia reacts with the molecule at carbon 2 to create the intermediate shown on the right side of the reaction arrow in reaction **C**. However, when an oxygen AND a double bond is added as shown in reaction **D**, ammonia reacts at carbon 2 AND carbon 4.



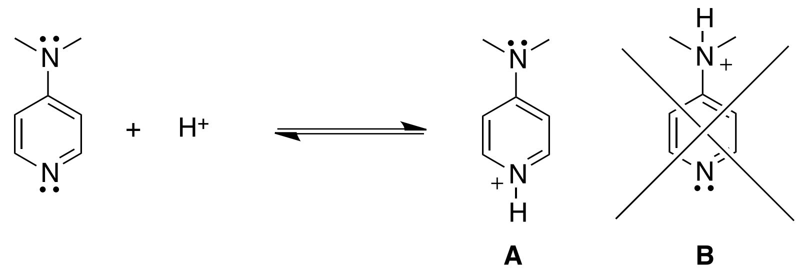
Question 1. Why doesn't ammonia react with the hydrocarbons as shown in **A** and **B**?

Question 2. Why is ammonia attracted to carbon 2 as shown in reaction **C**?

Question 3. Why is ammonia ALSO attracted to carbon 4 as shown in reaction **D**? Hint: Draw a resonance structure of the oxygen-containing starting material in reaction **D**.

Example 3.

Dimethylaminopyridine, commonly known as DMAP, reacts with acid (shown below as simply H^+) to give product **A** while producing NONE of **B**.

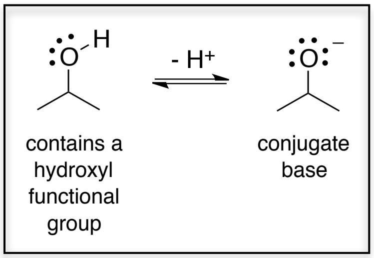


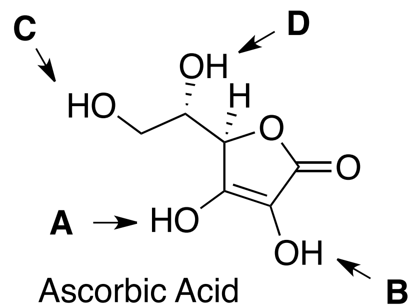
Question 1. Draw a curved arrow showing the attraction and thus bond making between the reactive nitrogen and the proton (H^+).

Question 2. Both nitrogens have an available lone pair of electrons, but why does only ONE of the nitrogens react?

Example 4.

When a hydroxyl functional group acts as an acid and donates a proton (H+), the oxygen of the resulting conjugate base will become negatively charged and will hold three lone-pairs of electrons. Of the four hydroxyl groups on ascorbic acid, **A** is the most acidic; describe why (be specific). Use resonance theory/structures to explain this. (this question was on last year's second exam!)

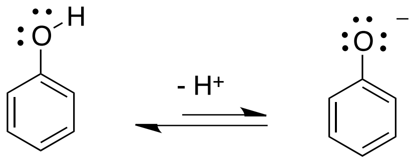




Ascorbic Acid

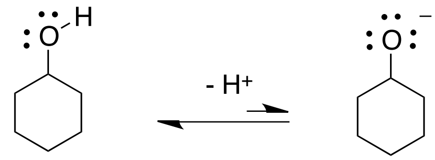
Example 5.

In comparison to cyclohexanol, phenol is a much stronger acid. This means that the conjugate base of phenol is more stable (lower energy) than the conjugate base of cyclohexanol (less stable, relatively high energy). Use resonance theory/structures to explain this.



phenol

pKa = 10

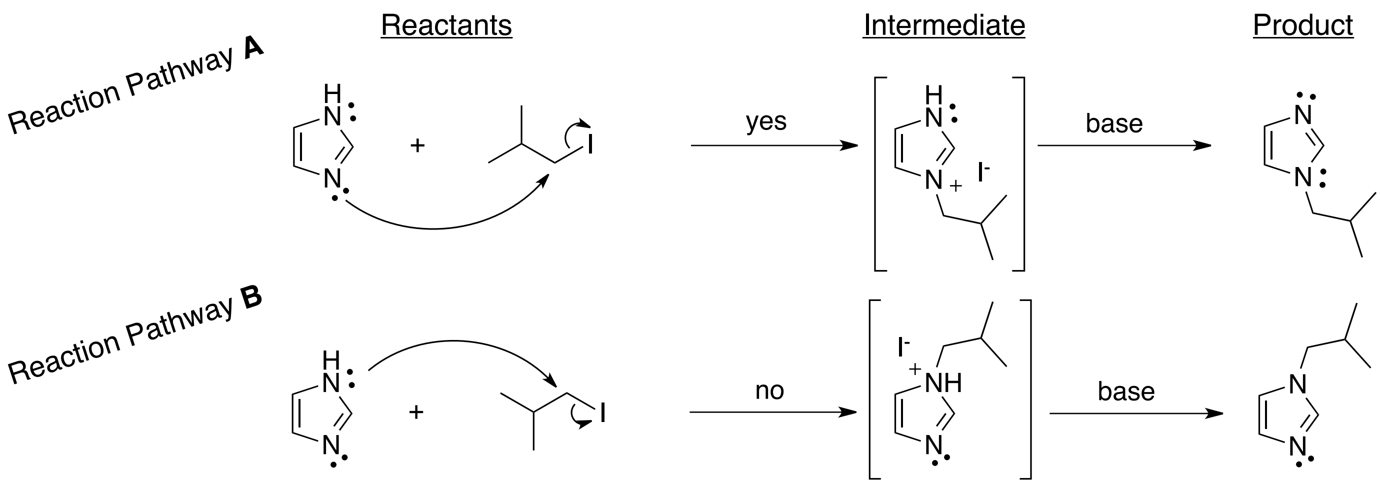


cyclohexanol

pKa = 16

Example 6.

Each of these reactions below represent an S_N2 alkylation reaction between imidazole (the nitrogen-containing molecule) and isobutyliodide.



Although these reactions appear quite similar, treatment of imidazole with isobutyliodide follows reaction pathway **A** - not **B**. Use resonance theory/structures to explain this.

Example 7. (this one is a bit more challenging)

Acetophenone is drawn below. Using a Nuclear Magnetic Resonance spectrometer (NMR), it can be shown that the six carbons that make up the benzene ring are not all magnetically unique; in fact there are four unique carbons - they are labeled **a**, **b**, **c** and **d**. What can also be determined from the NMR data is that carbons **a**, **b** and **d** are electron deficient (meaning they have a partial positive charge) when compared to the carbons labeled as **c**. One can argue carbon **a** is electron deficient because of an inductive effect (the carbonyl oxygen is pulling electrons toward itself; through-bond communication). Using resonance theory/structures, explain why carbons **b** and **d** are electron deficient when compared to **c**.