Nitrogen Centered Radicals

Organic Cumulative Exam
Saturday, December 4, 1999
9:00 AM- 12:00 noon
209 Schlundt

NAME:_____

1. Give a general example of how one would prepare each of the following radicals.

      a) Aminyl Radical

      b) Iminyl Radical

      c) Amidyl Radical

2. The following are rate constants for the abstraction of hydrogen from tributyltin hydride at 50°C. How can you rationalize these observed rate contants?

| $R_3C\bullet$	$R_2N\bullet$	$RO\bullet$
$k = 3 \times 10^6$	$k = 8 \times 10^4$	$k = 2 \times 10^8 \ M^{-1}S^{-1}$

3.   The Hammett values for the addition of aminyl radicals, aminium cation radicals and metal complexed aminyl radicals to substituted styrenes are 0.69, -1.29, and -0.98 respectively. Based on the data, what is the electronic nature of the respective radicals? (i.e. nucleophilic or electrophilic?). Please be specific, what do the Hammett values tell us about the effect of substituents on the addition of the radicals to the styrenes.

R\N/R   aminyl   = +0.69

R\N/R   aminium cation   = -1.29
 |
 H

R\N/R   metal complexed aminyl   = -0.98
 |
 M
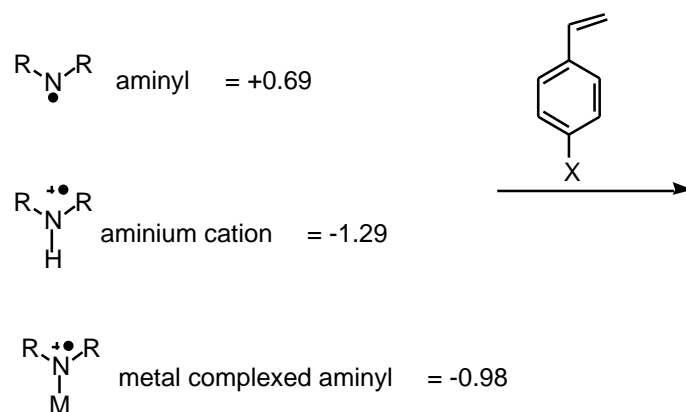
4.   For the following transformation: Provide a complete step-by-step mechanism for each step from **1** to **3**. Neatness is important. (*SynLett* **1996**, 1148)
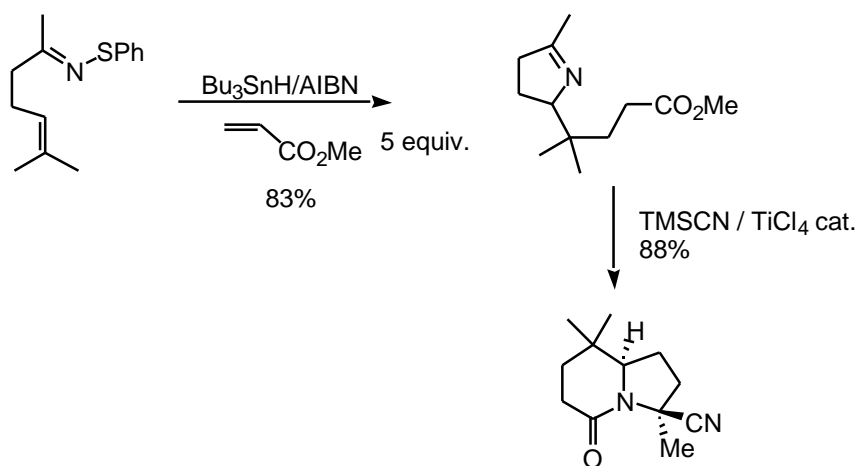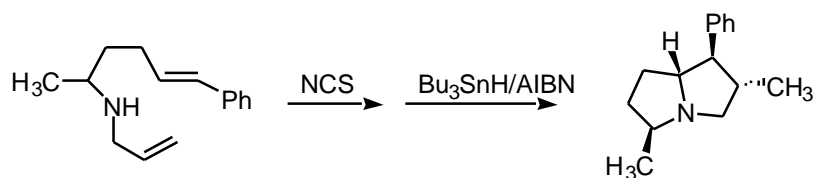

B.   Why are a large excess of methacrylate and the slow addition of tributyltin hydride necessary for the successful formation of **2**?

5.	Predict the product and provide a reasonable mechanism for the formation of your predicted product in the following reaction. (Hint: the product has a tricyclic 5,6,4 skeleton) *JACS* **1991**, *113*, 1055.
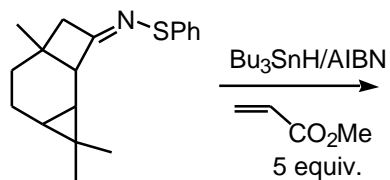
6.	Rationalize the stereochemistry observed in the major product obtained from the following aminyl radical cyclization. *Tetrahedron* **1999**, *55*, 6465.

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