Chemistry 310
Prof. B. Hanson
Spring 2018

Name: KEY

Exam #1

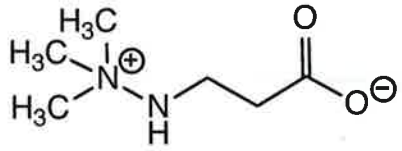
1.	_____	25 pts
2.	_____	25 pts
3.	_____	25 pts
4.	_____	25 pts
		100 pts

Science, after all, is a quest, and as such it's one of the oldest and most enduring stories we have. It's about searching for answers, struggling with setbacks, persevering through tedium and competing with colleagues all eager to put forth their own ideas about how the world works. Perhaps most of all, it's about women and men possessed by curiosity, people who devote their lives to pursuits the rest of us find mystifying or terrifying – chasing viruses, finding undiscovered planets, dusting off dinosaurs or teasing venomous snakes.

The Science and Art of Science Writing
Michelle Nijhuis *NYT* December 9, 2013

Mechanisms should include mechanistic arrows, lone pairs on all atoms that are giving or receiving electrons, formal charges where appropriate, any intermediates and of course, representative and relevant resonance forms when they help to explain the observed reactivity. If cofactors are involved, you must show the "business end" of the cofactor structure (the part that is reacting).

1. (25 points). Meldonium has been in the news recently as a Russian curler was caught doping with it. The structure is shown below.



meldonium

(a) What is the pK_a of typical ammonium ions? 9-12

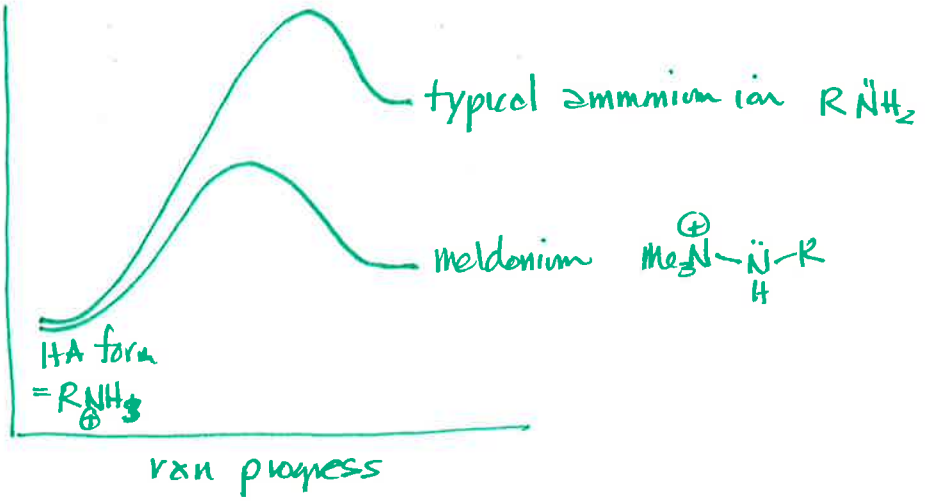
(b) Draw and balance the reaction of meldonium *in its ammonium form* acting as an acid.

5 pts each

(c) Would you expect the pK_a of the ammonium group in meldonium to be higher or lower than a typical ammonium ion? Circle higher or lower.

(d) Draw and label on a *single energy diagram* a typical ammonium ion acting as an acid, along with meldonium in its ammonium form acting as an acid. Put the acid forms at the same energy level.

regardless of your answer to (c), this diagram should be consistent



(e) Succinctly explain your answer to (c). No rambling!

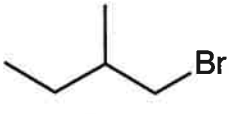
Protonated meldonium should be extremely eager to get rid of its proton as there are two + charges adjacent, which is very unstable/high energy. Therefore the pKa should be lower than typical ammonium ions. An argument can be made that it should be extremely acidic, possibly more acidic than the carboxylic acid

2. (25 points).

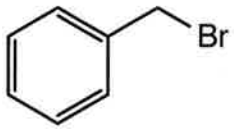
(a) Rank the following molecules with respect to the stability of the carbonium ion formed when the leaving group departs. 1 = most stable. No explanation required.

1 has resonance
2 is 2°
3 is 1°

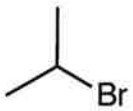
5 pts



3



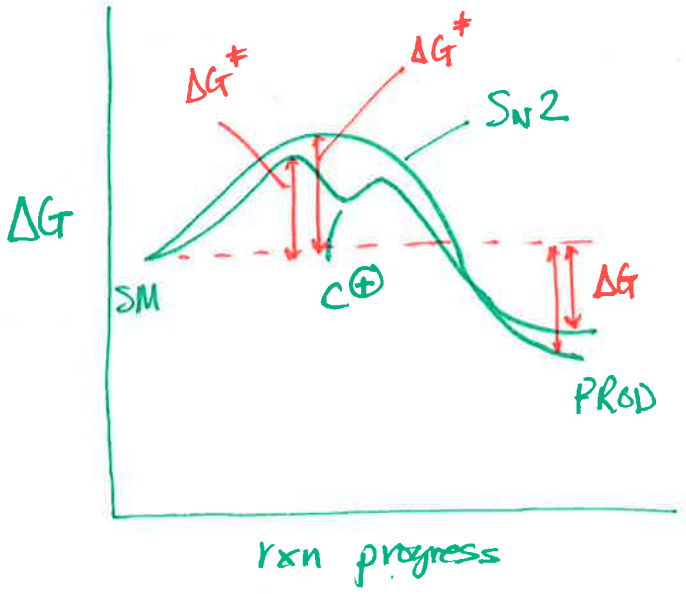
1



2

(b) Draw and completely label a *single* energy diagram which compares the S_N mechanisms.

10 pts each



Missing ΔG or ΔG‡, −2 pts each
C⊕ not labeled, −2 pts

3. (25 points) For the following scheme:

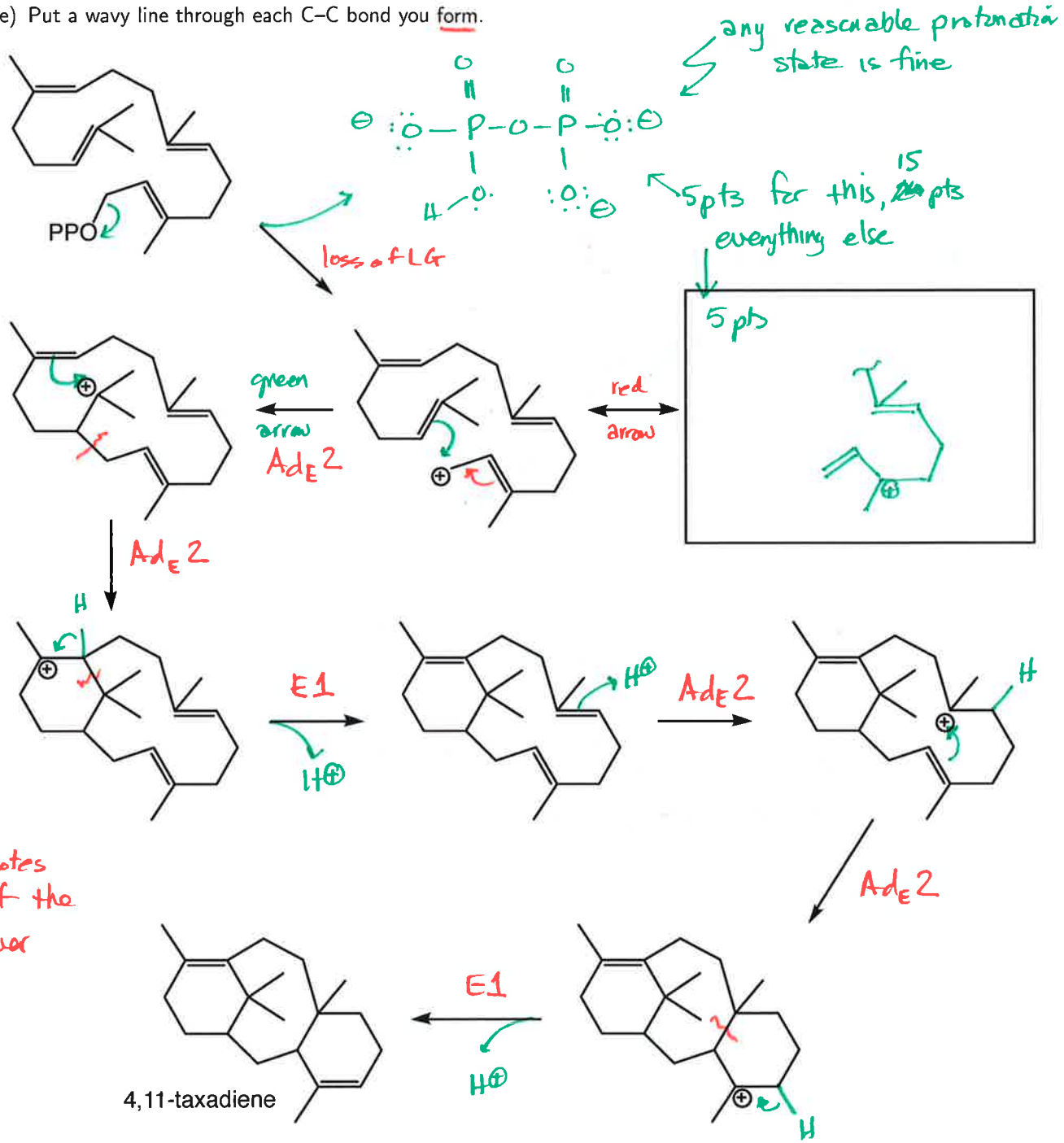
   (a) Add mechanistic arrows wherever needed.

   (b) Fill in the missing structure.

   (c) Balance each step (this should come from drawing the mechanism; other than "PPO", only H^+ is given off or consumed).

   (d) Draw out the complete structure of whatever "PPO" becomes.

   (e) Put a wavy line through each C–C bond you form.



mechanism notes not part of the req'd answer

4. (25 points). Part of the pathway leading to proline is shown below. Draw a reasonable mechanism for the entire pathway, in the process filling in the missing structure.