

Exam 2
Chem 21
Oct 21, 2009

Name Gary Snyder

page 1 (30) _____

2 (50) _____

total (200)

3 (30) _____

4 (40) _____

chk

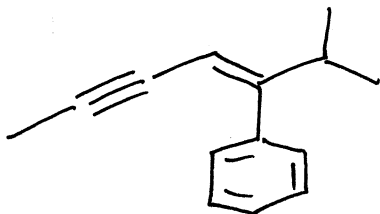
5 (30) _____

6 (25) _____

Please don't write in this space.

1. (30 points) Draw the following compounds in skeletal notation. Don't abbreviate substituents. Show stereochemistry clearly where necessary.

(a) (Z)-6-methyl-5-phenyl-4-hepten-2-yne

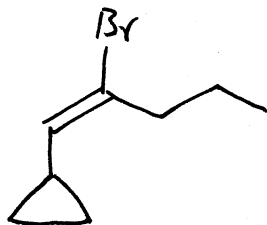


(b) *trans*-4-isopropyl-1,3-dimethylcyclobutene



either
enantiomer
ok, of course

(c) (*E*)-2-bromo-1-cyclopropyl-1-pentene

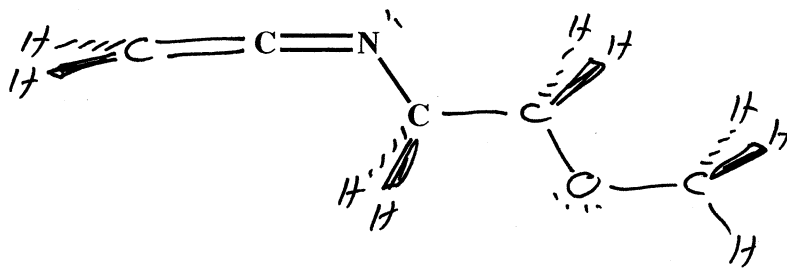


(d) *cis*-1-*tert*-butyl-3-chlorocyclohexane
in its most stable conformation



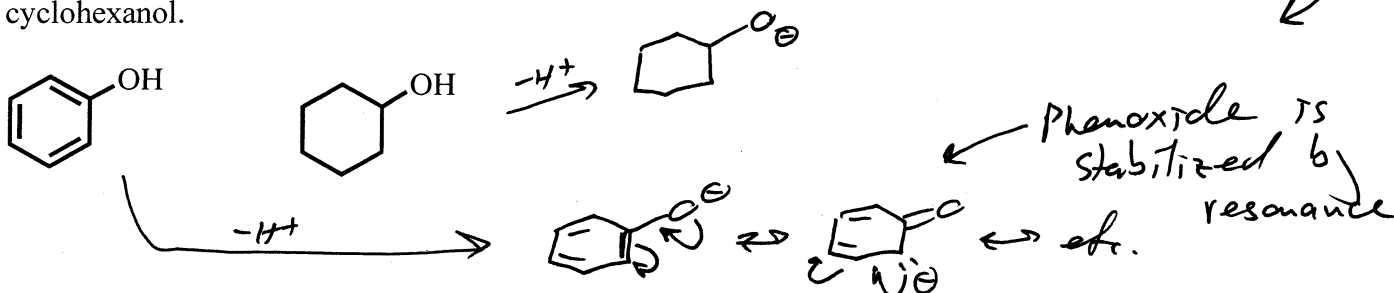
either
enantiomer
ok.

2. (15 points) Draw $\text{CH}_2=\text{C}=\text{N}-\text{CH}_2\text{CH}_2\text{OCH}_3$, so as to clearly show the complete 3-dimensional structure of its most stable conformation. Please add on to the CNC fragment provided.

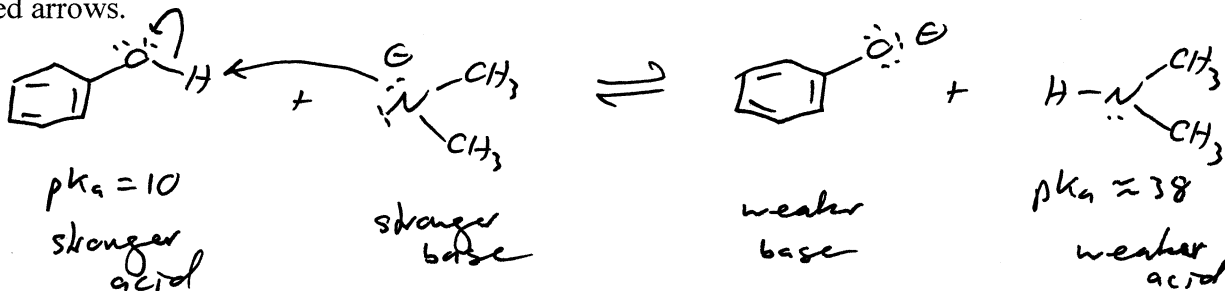


combination of 2 HW problems
wasn't this also an HW prob?

3. (35 points) (a) Explain *briefly* why phenol (below ^{left} ~~right~~, $\text{pK}_a = 10$) is a stronger acid than cyclohexanol.



(b) Write the acid-base reaction of phenol with $\text{NaN}(\text{CH}_3)_2$. Illustrate the reaction clearly with curved arrows.



(c) Label the acids with their pK_a values.

(d) Label the stronger and weaker acids, and label the stronger and weaker bases.

(e) Based on your labels, does the equilibrium lie to the left or the right?

(f) Based on your answer to part e, what is K_{eq} ?

10^{28}

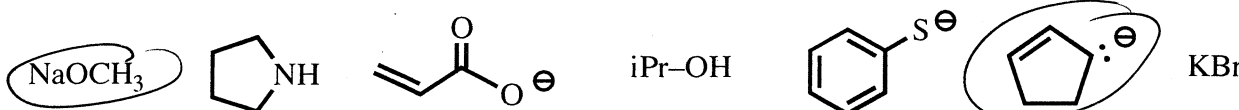
- right ->

(g) Based on your answer to part f, what is the approximate ΔG° for the equilibrium in kcal/mol?

$28 \times 1/3 \dots \text{damn, it's } \sim -37 \text{ kcal/mol}$

all answers must be consistent with previous part!

(h) Which of the following *bases* are strong enough to completely deprotonate phenol? (circle)

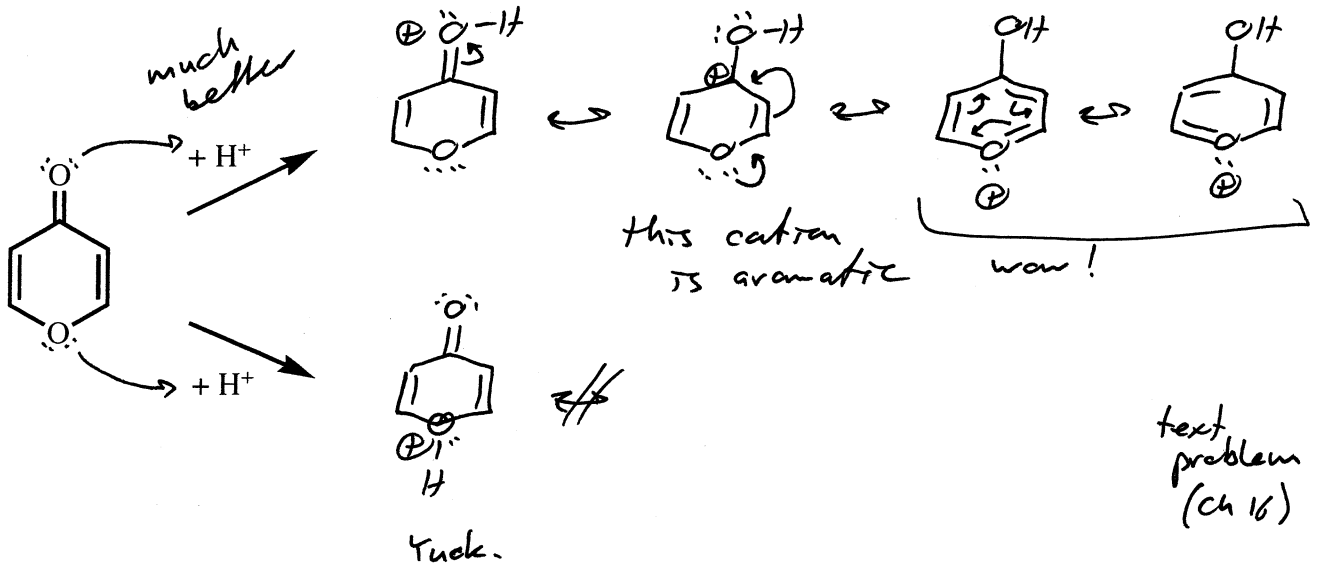


conj. acid pK_a : 16

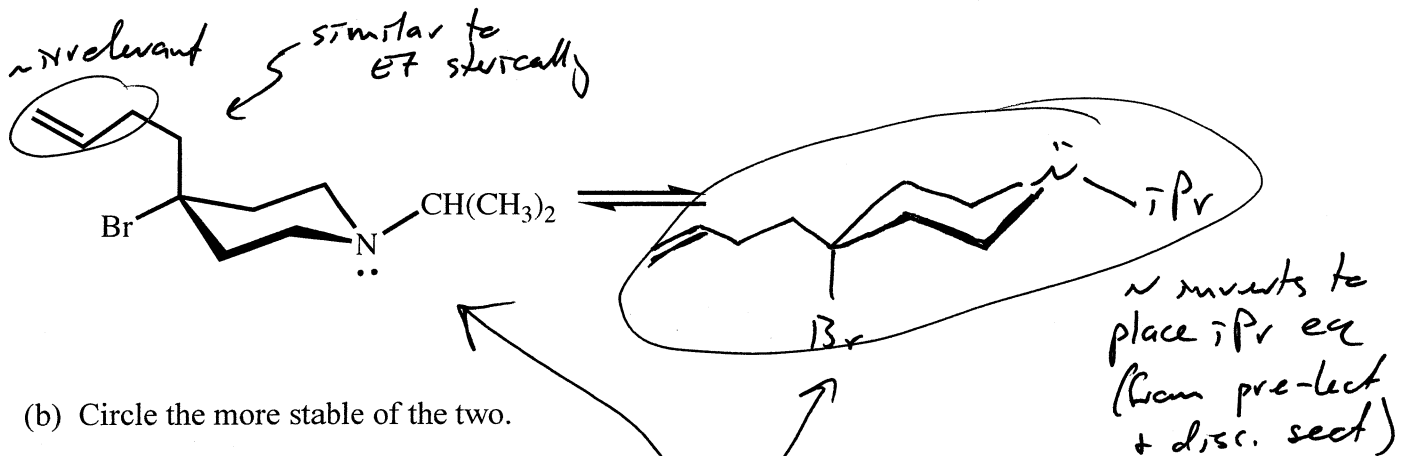
need base with conj. acid $\text{pK}_a > 10$

low (17 Br!)
page 2

4. (15 points) In principle, the compound below can be protonated on either oxygen. But one oxygen is much more basic than the other. Draw the two conjugate acids that could be formed, and decide which protonation is the more favorable. Briefly explain your choice.



5. (15 points) (a) One chair conformer of a substituted piperidine is shown below. Draw the other chair conformer.



(b) Circle the more stable of the two.

(c) Use the data in the table at the right to estimate ΔG° for the ring flip above. Make sure your reasoning is clear

steric strains: $\sim 1.8 + 0.5$
(ax substituents)

$$\Delta G^\circ = -1.3 \text{ kcal/mol}$$

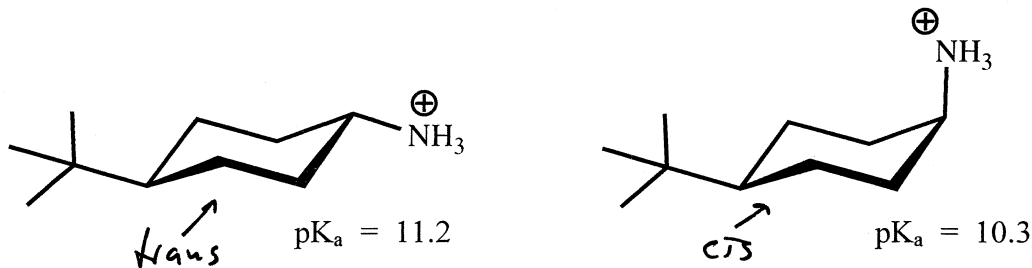
	\rightleftharpoons	
R = Me	$\Delta G^\circ = 1.7$	kcal/mol
R = Et	1.8	
R = iPr	2.2	
R = t-Bu	5.0	
R = CN	0.2	
R = vinyl	1.7	
R = Br	0.5	
R = NH ₂	1.4	

(d) so what's K_{eq} ?

$$K_{eq} \approx 10 \quad \therefore \sim 10\% : 90\% \text{ at equilib.}$$

I should have left this part in!

6. (12 points) Two isomeric cyclohexylammonium ions are shown below.

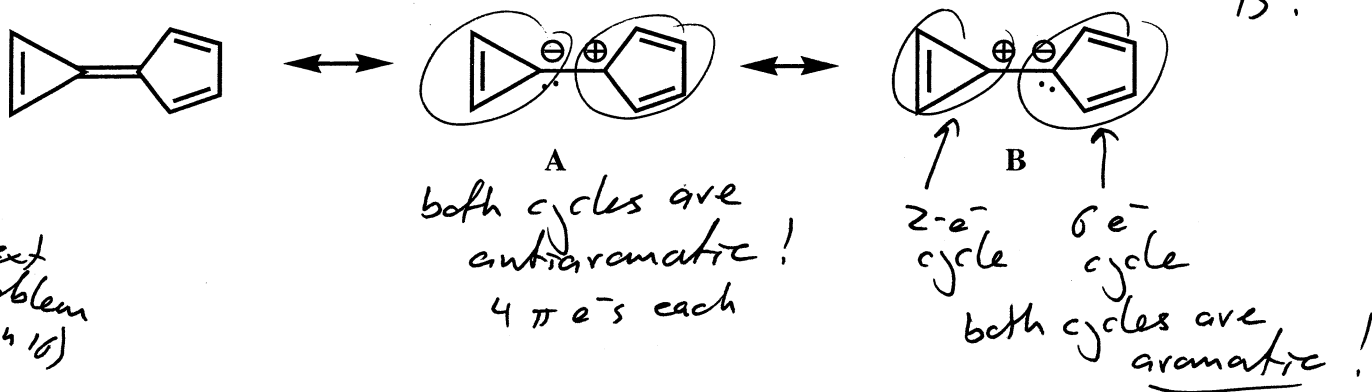


(a) Label them *cis* and *trans*.

(b) Explain briefly, in terms of structure, why one stereoisomer is more acidic than the other.

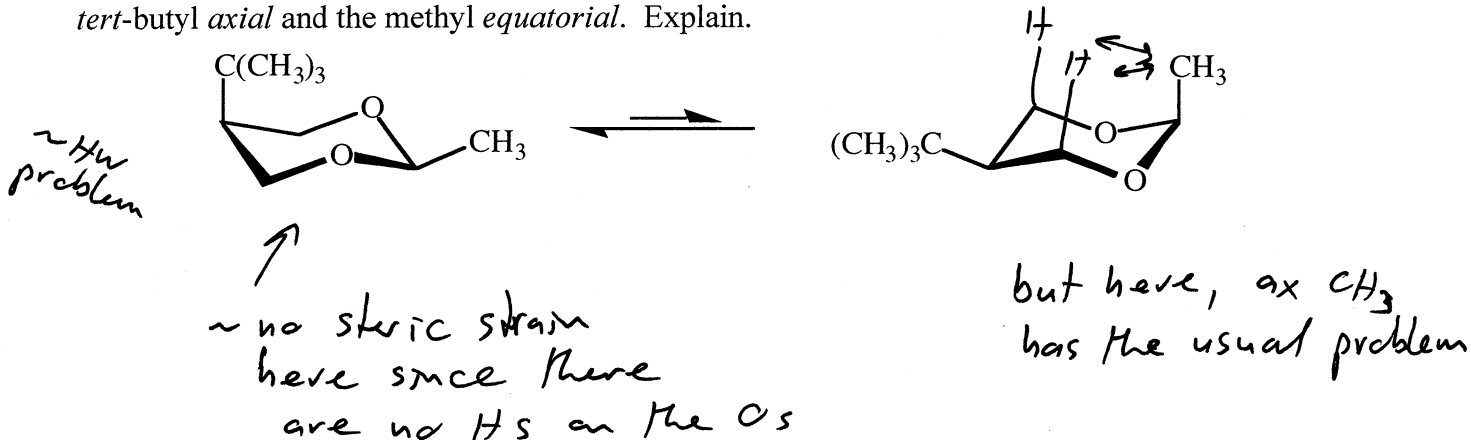
stronger acid
 loss of an H^+ reduces the steric strain caused by the axial $-NH_3^+$ (i.e. $-NH_2$ is less sterically demanding).

7. (15 points) Calicene has been found experimentally to have a surprisingly large dipole moment. This can be attributed to a contribution from minor charge-separated resonance structures like A or B. (Of course, the charge can be further delocalized in each case.) Which polarization is the more important (A or B)? Briefly explain your choice.



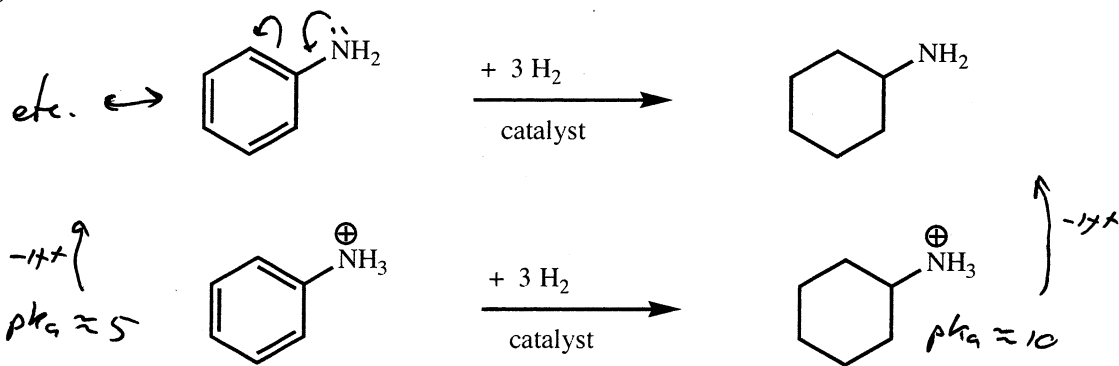
text problem (ch 16)

8. (13 points) In contrast to the corresponding cyclohexane (*cis*-1-*tert*-butyl-4-methylcyclohexane), the lower energy chair conformation of the dioxane below is the one with the *tert*-butyl axial and the methyl equatorial. Explain.

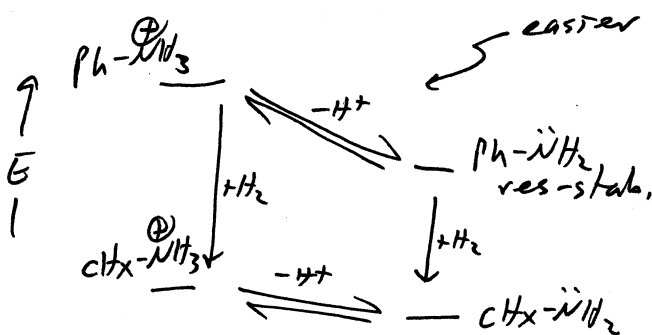


\sim HW problem

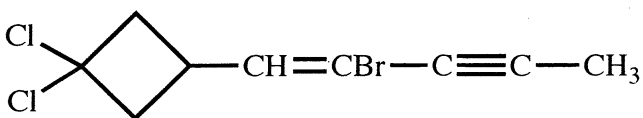
9. (15 points) Which of the two hydrogenations below would you expect to be the more exothermic? Explain your choice. (hint: the pK_a of Ph-NH_3^+ is about 5; that of cyclohexyl- NH_3^+ is about 10.)



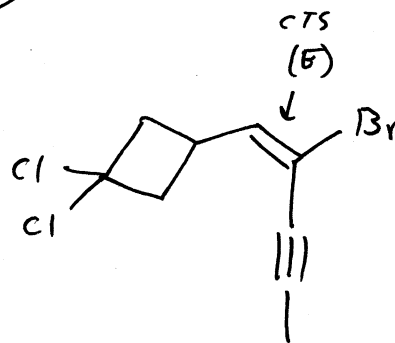
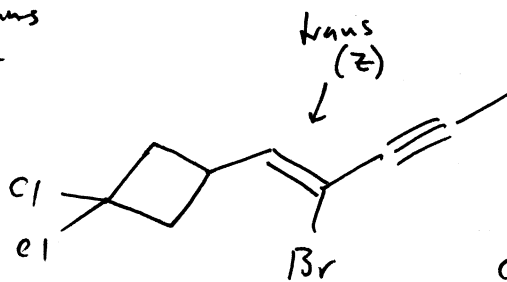
This pK_a is lower mainly because aniline is stabilized by resonance, so the second hydrogen should be more exothermic



10. (15 points) Draw all the stereoisomers of the following compound. No need to show the conformation, just be sure that the stereochemistry is clear.

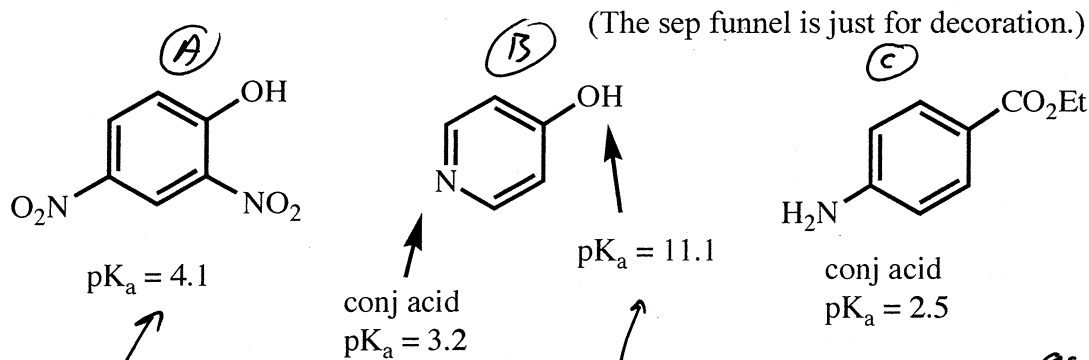
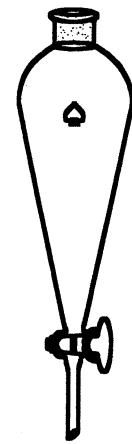


no cis/trans issue here



11. (25 points). Write a flow chart for the separation of the three compounds below using liquid-liquid extraction. Draw structures to clearly show what compound is present at each step of the process *and its protonation state*.

Assume that the mixture is dissolved in diethyl ether, Et_2O , to begin. In addition to water, your lab is stocked with aqueous HCl , aq NaOH , and aq NaHCO_3 (pK_a of H_2CO_3 is 6.3).



can deprotonate with HCO_3^-
(like we do with a carbox acid!)

can deprot. with HO^-

aq acid probably won't help us here.

Et_2O soln to start

