Chem 221 F08 Sect 01 Dr. C. Rogers **NAME:** Rogers
ANSWER KEY

INTRODUCTORY ORGANIC CHEMISTRY I --- PROBLEM SET #1

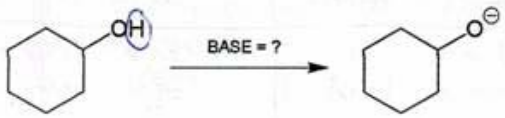
INSTRUCTIONS: ANSWER ALL QUESTIONS ON THESE PAGES. HAND IN (stapled, with no extra pages please) AT THE BEGINNING OF CLASS on Thursday Oct.2nd. LATE SUBMISSIONS WILL NOT BE ACCEPTED (EARLY IS FINE). ALL MATERIAL CAN ALL BE FOUND IN THE CLASS NOTES AND IN BRUICE CHAPTERS 1, 2 & 7.

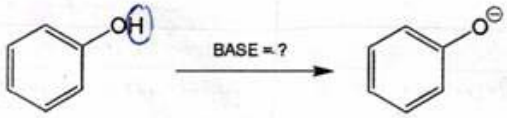
 # 1. For each of the reactions below, list all the bases (from the table) that would be strong enough to perform the indicated deprotonation.

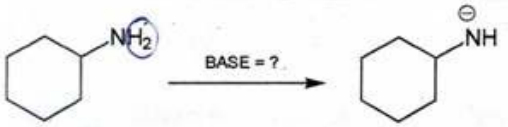
Available bases	pKa of conj. acid
$(CH_3CH_2)_2NH$ / R_2NH_2	~11
NaOH ($OH^\ominus$) / H_2O	15.7
NaH ($H^\ominus$) / (pK_a of H_2 is 35)	
$NaOCH_2CH_3$ / EtOH	16.0
$NaNH_2$ ($NH_2^\ominus$) / NH_3	36

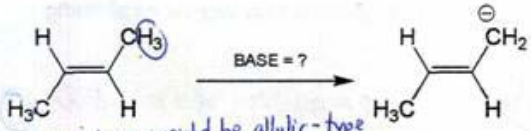
How to do this problem: Our base must be a stronger base than the anion we are trying to prepare in the rxn. Thus, our base's conjugate acid must have a larger pKa (weaker acid) than what we are trying to deprotonate.

approx. pKa

16  WHICH BASES WOULD WORK: NaH, $NaNH_2$

10  all of them

40  none of them!

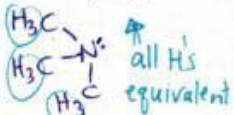
41?  none of them!

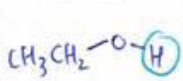
conj. base would be allylic-type anion (resonance-stabilized)

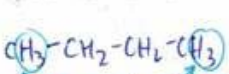
 # 2. Circle the most acidic H in each compound below, then rank the compounds in order of increasing acidity (put the most acidic one on the right-hand side). Briefly justify how their structures allowed you to make this decision (point form only, please). Then, look up their pK_a values (see Bruice Appendix II) and verify that the pK_as are consistent with your ranking and explanation....

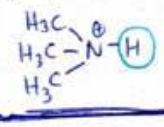
only compound not found (nor anything close ...)

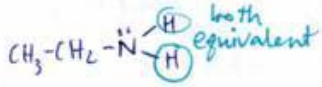
i.e.: stronger acid should have lower pKa ✓

$(CH_3)_3N$  all H's equivalent

CH_3CH_2OH 

$CH_3CH_2CH_2CH_3$  or other end

$(CH_3)_3NH^+$ 

$CH_3CH_2NH_2$  both equivalent

RANKING: $CH_3CH_2CH_2CH_3$ < $(CH_3)_3N$ < $CH_3CH_2NH_2$ < CH_3CH_2OH < $(CH_3)_3NH^+$ most acidic

1. how H chosen
2. how ranking chosen
3. pKa... matches?

$CH_3CH_2CH_2CH_3$:
1. 1° CH more acidic than 2°, because 2° CH's conj. base has EDG alkyl groups, which destabilizes its conj. base more
2. sp^3 CH's are WEAK acids!

pKa > 60 ✓

$(CH_3)_3N$:
1. all H's equivalent here...
2. N acts as EWG + stabilizes conj. base here (making conj. acid more acidic, relative to $CH_3CH_2CH_2CH_3$)

40 < pKa < 60 ✓

$CH_3CH_2NH_2$:
1. H on nitrogen, more electroneg. than C
2. N less electroneg. than O, so conj. base of amine is less stable (more basic) than conj. base of alcohol.

pKa ≈ 40 ✓

CH_3CH_2OH:
1. H on oxygen, more electronegative than Carbon
2. and, O more electroneg. than N...

pKa = 16 ✓

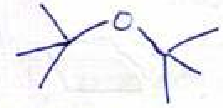
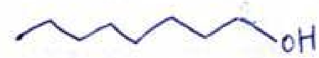
$(CH_3)_3NH^+$:
1. H on N, more electroneg. than C
2. positive N's have weaker hold on H than neutral N or O does.

pKa = 10.6 ✓

Rogers

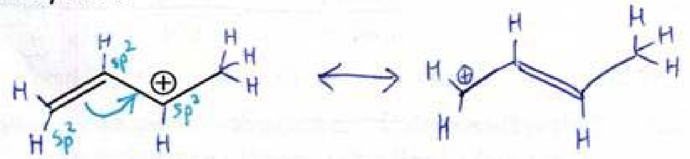
Chem 221 W08 Sect 52 Dr. C. Rogers isomers ($C_8H_{18}O$) **NAME:** ANSWER KEY

 # 3. Draw line (skeletal) structures of the following compounds and rank them in order of increasing boiling point. Explain your choice briefly. COMPARE STRENGTH OF INTERMOLECULAR FORCES.

	(lowest b.p.) $(CH_3)_3COC(CH_3)_3$	$CH_3(CH_2)_3O(CH_2)_3CH_3$	$CH_3(CH_2)_7OH$ (highest Bp.)
WHY?			
London forces?	• bulky t-butyl groups ∴ less surface to contact	• long chains ∴ lots of points of contact	• long chain ∴ lots of points of contact
Hydrogen bonding?	• no hydrogen bond donors ∴ no hydrogen bonding	• no hydrogen bond donors... ∴ cannot hydrogen bond	• can also hydrogen bond –ÖH is acceptor –OH is donor
dipole-dipole?	• weak, near O–C only	• weak, near O–C only	• stronger, near H–O–C ...
RESULT	weakest forces	stronger London forces...	strongest London AND H-bonding

REALLY: bp 107°C bp 142°C bp 196°C

 # 4. Which of the following species is resonance-stabilized? For those that have resonance, draw the resonance structures...and for those that don't have resonance, provide a few words explaining why they don't.

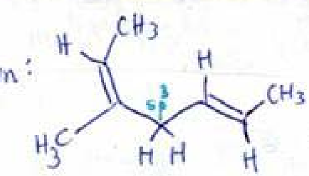


Resonance-stabilized ✓.
3 sp^2-C's in a row
∴ 3 p orbitals in a row
∴ delocalized π-electrons.

$$\begin{matrix} CHCH_3 \\ \| \\ CH_3CCH_2CH{=}CH\ CH_3 \end{matrix}$$

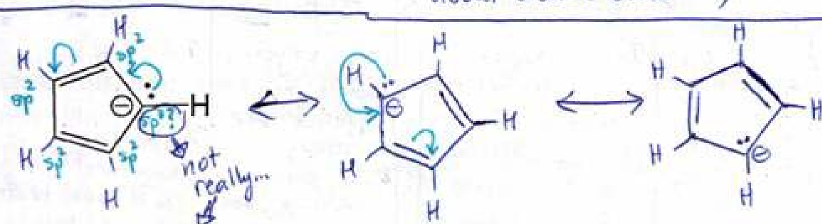
fixed typo... ⇓

redrawn:



(or with other geometries about double bonds...)

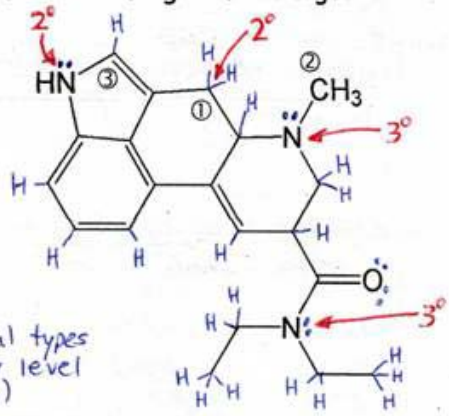
There is an sp^3 C in between the 2 sets of sp^2-C's
∴ the 2 π systems are isolated from each other.
∴ NOT resonance-stabilized.



• lone pair on atom adjacent to π system CAN make atom "rehybridize" to sp^2.

Resonance-stabilized ✓
4 sp^2-C's in a row
AND
a lone pair on next atom in row (adjacent)
∴ lone pair's atom rehybridizes to be sp^2 to allow for delocalization (favourable)

 # 4. Lysergic acid diethylamide (LSD), shown here, is a hallucinogenic substance known on the street as "acid". It is a synthetic derivative of a natural compound found in a fungus of the ergot family. Answer the following questions about this molecule:



a) Draw on all "implied" hydrogen atoms and lone pairs.
(in blue pen...)

b) Which orbitals are involved in the σ-bond between the carbonyl carbon and the attached ring?
σ bond: $2sp^2$ — $2sp^3$ } indicates orbital types + their energy level (i.e. n=2 shell)
carbonyl C ↖ ↗ ring C

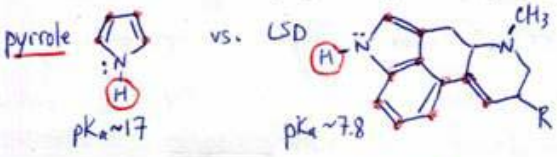
c) Label the N atoms and the three numbered C atoms as 1°, 2°, 3° as appropriate.
(in red pen) bonded to 1 C ⇒ 1° primary
2 C ⇒ 2° secondary
3 C ⇒ 3° tertiary
tricky, ∴ not counted { Note: C② is a METHYL C (not 1°)
C③ is a VINYL C (not 1°)

d) Consider the C-H bonds on the three numbered atoms. Which of those C-H bonds would be the longest? Why? C① - H.
Consider the orbitals involved: (+ remember: more s-character means smaller ∴ shorter bond...)
C① - H σ: $2sp^3$ - 1s (25% s, 75% p) } same s-character ∴ similar length
C② - H σ: $2sp^3$ - 1s } same s-character ∴ similar length
C③ - H σ: $2sp^2$ - 1s (33% s, 67% p) } most s-character ∴ shortest bond.
The only difference between the C①-H and the C②-H bonds is the fact that the C② is also bonded to N. This might introduce slight polarity to the C②-H bond, which would increase its strength + shorten it slightly.

Now consider the acid-base properties of this molecule.

a) The pK_a of the most acidic hydrogen in LSD, the amino group NH shown above, is unusually low (around ~7.8). Using Appendix II in the Bruice text, find (and draw) the small molecule that has a nitrogen atom in a similar environment with pK_a ~17.

1. Based on these pK_a values, which of these two molecules is easier to deprotonate? (means "remove H^+ from...")



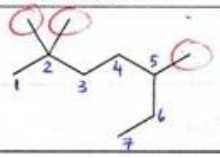
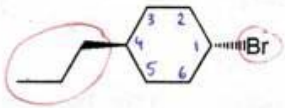
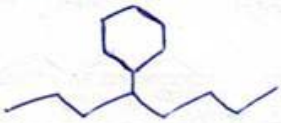
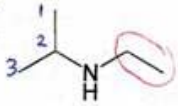
Lower pH means stronger acid, so the LSD's NH group should be easier to deprotonate than pyrrole's.

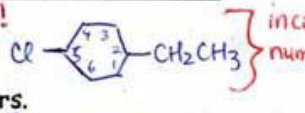
2. Why are these two N-H's pK_a values so different? ⇒ Larger extent of electron delocalization. In the LSD molecule, there are 10 sp^2 C's in a row/cycle (marked above with red •) that permit electron delocalization (i.e. overlapping p orbitals ⇒ resonance...). In the smaller molecule (called pyrrole), there are only 4. For both molecules, these "extended π-systems" make the conjugate base form (deprotonated, $N:^{\ominus}$ form) more stable than expected, so the NH's are more acidic than expected ("normal" amines' pK_a ~40!)

b) Based on LSD's pK_a, do you think this substance deserves its street name of "acid"? That is, would it produce a detectably acidic solution if dissolved in tap water at pH ~5.5? Explain. YES.
Just wanted you to THINK about this...
pK_a 7.8 means at pH 7.8, the substance would be 50% deprotonated. At pH 5.5, much less deprotonated form would exist. The equilibrium shown below would lie predominantly to the LEFT... but... there would still be some molecules which do react, so some extra H^+ would be added to the solution, making it more acidic. Note that if you arbitrarily choose an initial LSD-NH concentration of say 0.10M, + if you do an equilibrium calculation (like in Chem 206), you will see the pH drop from this.

$$LSD\text{-}NH + H_2O \rightleftharpoons LSD\text{-}N^{\ominus} + H_3O^+$$ (↖ lowers pH.)

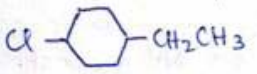
 # 5. Complete the following table.

Systematic (IUPAC) name	Line (skeletal) structure
7 C chain ⇒ a heptane... 3 methyl substituents: on C2, C2, C5 ⇒ 2,2,5-trimethylheptane	
cis-1-ethyl-3-methoxycyclopentane ($-CH_2CH_3$, $-OCH_3$, ⬠)	
6 C ring ⇒ a cyclohexane... bromo, propyl } 1,4 relative to each other (+ trans!) ∴ lowest in alphabet ⇒ gets lower # ⇒ trans-1-bromo-4-propylcyclohexane	
4-cyclohexyloctane (substituent; main chain (parent))	
longest chain with N attached = propyl (3C) ⇒ propanamine... other group attached to N = ethyl (2C) ⇒ N-ethyl... ⇒ N-ethyl-2-propanamine OR N-ethyl propan-2-amine	

 # 6. Consider this incorrectly named molecule: "2-ethyl-5-chlorocyclohexane". incorrect alphabetization!  incorrect numbering!

a) Write the correct name for this molecule, and draw its two geometric isomers.

1-chloro-4-ethylcyclohexane

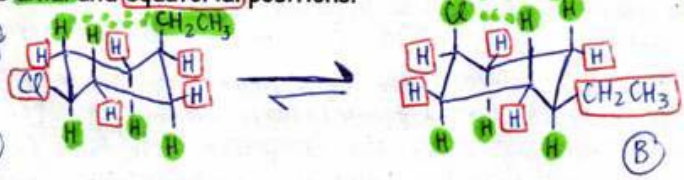


cis  (or, both as ||||)

trans  (or Cl|||| and ⬅CH_2CH_3)

b) Draw the chair-chair interconversion (ring-flipping) equilibrium for the *cis* isomer of this molecule, and label all the axial and equatorial positions.

The 1,4 relative positions of cis Cl + Et mean that 1 must be axial + 1 equatorial.



Cl and CH_2CH_3 must both point either "up" or "down" (here: both "up" shown)

c) In an equilibrium sample of this substance, which conformer from (b) would another molecule be most likely to collide with? Why?

Another molecule is more likely to collide with the MORE STABLE CONFORMER, because that is what most of the 1-chloro-4-ethylcyclohexane molecules would look like at any given moment. Collisions occur on a purely statistical basis: if [B] > [A], collide more with [B].

For the conformers shown above: the right-hand one (B) is more stable (ethyl equatorial).

Why: Ethyl groups take up more space (because they freely rotate) than monatomic Cl substituents. The 1,3-diaxial interactions (steric strain) are minimized if the larger group can be positioned in equatorial position rather than axial. Thus, Cl stays axial, Et equatorial.