

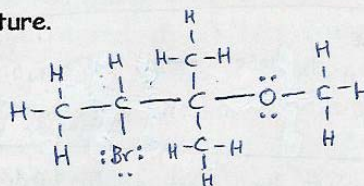
## INTRODUCTORY ORGANIC CHEMISTRY I --- PROBLEM SET #1

**INSTRUCTIONS:** HAND IN STAPLED, COMPLETED ASSIGNMENT (no extra pages please) AT THE BEGINNING OF CLASS on Thursday Sept. 29. LATE SUBMISSIONS WILL NOT BE ACCEPTED. YOU MUST ANSWER ALL QUESTIONS. NOT ALL THE MATERIAL HAS BEEN COVERED YET; IF NOT, IT WILL BE COVERED SOON IN CLASS.

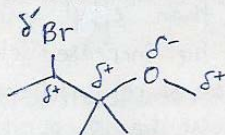
# 1. Consider the following condensed structural formula:  $\text{CH}_3\text{CHBr}(\text{CH}_3)_2\text{OCH}_3$

(a) Draw the molecule's complete Lewis structure.

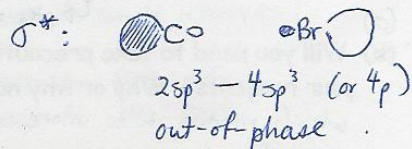
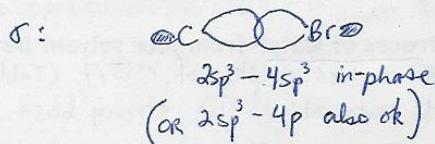
- show all bonds + lone pairs
- do not need to approximate the true geometry



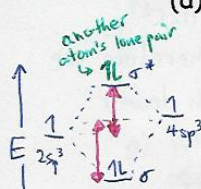
(b) Draw a skeletal (line) structure of the molecule. Label the molecule (using  $\delta^+$  &  $\delta^-$ ) to show the polarity of the bonds; do not include bond dipoles that would cancel out on average.



(c) Sketch and label the orbitals (valence bond theory style) to show the overlap involved in the C-Br  $\sigma$ -bond, and another picture showing the corresponding antibonding ( $\sigma^*$ ) orbital.



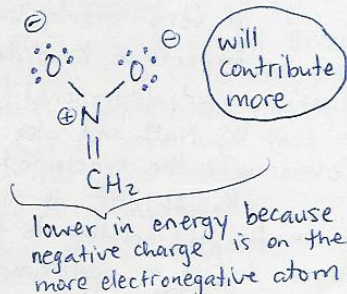
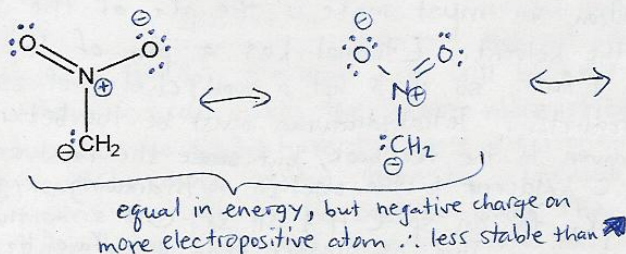
(d) What would happen to the C-Br  $\sigma$ -bond if another molecule collided with this molecule in a way that allowed a lone pair to enter the region of space defined by the  $\sigma^*$  orbital?



If lone pair enters the  $\sigma^*$  orbital, the energetic advantage of the filled  $\sigma$ -bond would be counteracted by the destabilization due to the filled  $\sigma^*$  orbital. The result is that the bond between the C + Br would break, and a new bond between the "other atom" and the carbon would form.

# 2. Complete the Lewis structure of the following closed-shell species (i.e., all atoms have full valence; you should add the lone pairs & any missing formal charges). Draw another closed-shell resonance contributor, and predict which species will contribute more to the character of the resonance hybrid.

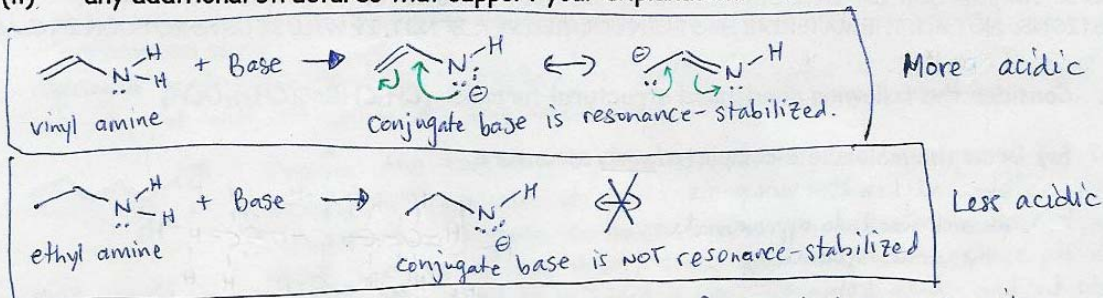
The more stable the resonance structure is, the more it contributes to the resonance hybrid (the real structure).



# 3. Which species is more acidic: vinylamine ( $\text{CH}_2\text{CHNH}_2$ ) or ethylamine ( $\text{CH}_3\text{CH}_2\text{NH}_2$ )?

Your answer should include a brief written explanation, and:

- (i) a structural diagram (Lewis or skeletal) of each acid & its conjugate base;  
 (ii) any additional structures that support your explanation.



In both amines, the most acidic hydrogen is one of the H's bonded to nitrogen, rather than an H bonded to carbon, because N is more electronegative than C and is therefore better able to stabilize the conjugate base's lone pair by holding it closer to the nucleus. Vinyl amine is more acidic than ethyl amine because the conjugate base's stability is further enhanced by resonance delocalization. Resonance occurs in the conjugate base of vinyl amine because the N rehybridizes to  $\text{sp}^2$  in order that the lone pair in its p orbital can be delocalized across the 2 p orbitals of the adjacent  $\pi$ -bond. This cannot occur in ethyl amine, because the adjacent C atom is  $\text{sp}^3$ -hybridized + has no unhybridized p orbitals to allow delocalization.

# 4. You wish to do a chemical reaction involving the *tert*-butoxide anion,  $(\text{CH}_3)_3\text{CO}^-$ , so you plan to treat *tert*-butanol ( $(\text{CH}_3)_3\text{COH}$ ) with sodium hydride (NaH).

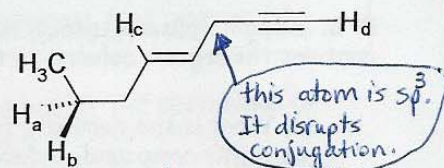
(a)  $\text{pK}_a = 18$   $\text{pK}_a = 35$  (see notes)

(b) Will you need to take precautions to remove traces of water from your solvent before adding your reagents? Why or why not? **YES.** Water has a  $\text{pK}_a$  of  $\sim 15.7$  (Table in Appendix II), which means it is more acidic than *t*-butanol. The strong base NaH will preferentially deprotonate the most acidic species it encounters, so we will need to remove the water from the solution. If we do not, the  $\text{H}^\ominus$  will react with  $\text{H}_2\text{O}$  (to form  $\text{OH}^\ominus$ ) rather than with *t*-butanol (to form *t*-butoxide), and therefore we would either get no *t*-butoxide formed at all, or we will get a much lower yield of it than expected.

(b) Which solvent would be better to use, and why? Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) or tetrahydrofuran?

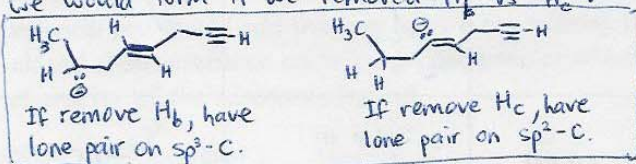
Both solvents would be able to solubilize *t*-butanol effectively, because both have nonpolar and polar regions, plus the capacity to hydrogen bond. However, our reaction involves ~~using~~ using a very strong base (NaH), + forming another strong base ( $\text{tBuO}^\ominus$ ). The most important consideration we must make is the  $\text{pK}_a$  of the solvent, so that we avoid deprotonating the solvent. Ethanol has a  $\text{pK}_a$  of 16, so would be deprotonated by NaH and also by  $\text{tBuO}^\ominus$ , so it is not a good choice of solvent, as it would react with the reactants/products. Tetrahydrofuran must be the better choice by default. The  $\text{pK}_a$  of THF is not given in the textbook, but ~~the~~ the most acidic H would be one of the H's bonded to the C adjacent to the electron-withdrawing oxygen. We may be able to deduce an approximate  $\text{pK}_a$  for an  $\text{sp}^3\text{-C-H}$ ; all  $\text{sp}^3\text{-C-H}$ 's in the appendix have  $\text{pK}_a > 40$ . This is greater than the  $\text{pK}_a$  of  $\text{H}_2$ , so  $\text{H}^\ominus$  cannot deprotonate THF.

# 5. Consider the four "H<sub>x</sub>" hydrogen atoms (labeled H<sub>a</sub>, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>) in the molecule shown at the right, and answer the following questions:



- a) Are the double bond and triple bond in this molecule **isolated** or conjugated? Explain. **Conjugated = delocalized; isolated = localized.**  
 Conjugated vs. isolated refers to whether or not the  $\pi$ -system is extended over many atoms (delocalized) or localized between only 2 atoms. An isolated  $\pi$ -bond is one that exists between 2 atoms with unhybridized p-orbitals oriented parallel so they overlap, but the neighbouring atoms to which these 2 atoms are bonded do NOT have unhybridized p-orbitals; this keeps the  $\pi$ -bond between 2 atoms only. In this molecule, the  $C=C$  and  $C\equiv C$  bonds are separated from each other by an  $sp^3$ -hybridized carbon, which has NO unhybridized p-orbitals. This prevents the two  $\pi$ -systems from being able to overlap with each other, because their p-orbitals can not span the distance across that  $sp^3$ -carbon. Thus, the 2 systems are **isolated**.
- b) What is the approximate bond angle of H<sub>a</sub>-C-H<sub>b</sub>?  
 $sp^3$  hybridized  $\therefore$  angle is  $109.5^\circ$
- c) Which C-H<sub>x</sub> bond should be the shortest?  
 $C-H_d$   $2sp-1s$  overlap vs.  $2sp^2-1s$  vs.  $2sp^3-1s$  } more s-character leads to shorter bond, since orbital is closer to nucleus
- d) Which C-H<sub>x</sub> bond should have the highest bond dissociation energy?  
 $C-H_d$  same reason as above; shorter bond is harder to break
- e) What is the approximate pK<sub>a</sub> of H<sub>a</sub>? } near 50 (comparable to simple alkanes)  
 H<sub>b</sub>? }  
 H<sub>c</sub>? near 44 (comparable to H<sub>2</sub>C=CH<sub>2</sub>)  
 H<sub>d</sub>? near 25 (comparable to HC≡CH)
- f) Which orbitals are involved in the  $\sigma$ -bond between C and H<sub>d</sub>?  
 $C 2sp - H 1s$
- g) Why is the pK<sub>a</sub> of H<sub>b</sub> higher than that of H<sub>c</sub>? In other words, explain what causes H<sub>c</sub> to be more acidic than H<sub>b</sub>.

To answer this, we must consider the nature + relative stabilities of the conjugate base we would form if we removed H<sub>b</sub><sup>+</sup> vs H<sub>c</sub><sup>+</sup>:



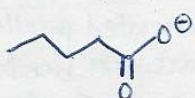
The conjugate base formed if H<sub>c</sub> were to be removed would be more stable, because the lone pair would reside in an  $sp^2$  orbital rather than an  $sp^3$  orbital. Because the  $sp^2$  orbital has 33% s-character, versus only 25% s-character for  $sp^3$ , the lone pair will be held more tightly to the nucleus of the  $sp^2$ -carbon, which makes the anion more stable. (It is often said that the more s-character the orbitals have, the more electronegative the atom ~~seems~~ seems.) Thus, the H<sub>c</sub> will be more acidic than H<sub>b</sub>, because the conjugate base is weaker. This means the pK<sub>a</sub> of H<sub>c</sub> will be lower than that of H<sub>b</sub>, because weaker acids have higher pK<sub>a</sub>s and stronger acids have lower pK<sub>a</sub>s.

explanations not required

# 6. Imagine you add a small amount of pentanoic acid,  $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ , to a separatory funnel that contains the organic solvent diethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ) and water at a pH of 7.0.

- (a) What is the dominant form of the acid after you mix the phases? Draw the line structure of this compound, and explain why the majority of the molecules are present in this "protonation state".

Because pentanoic acid is a carboxylic acid, its  $pK_a$  is  $\sim 5$ . Thus, at a pH of 7, it will exist in its deprotonated, conjugate base form:



Mixing the two layers exposes all the substances to the same pH, because the molecules of pentanoic acid, ether and water will all be brought into intimate contact. The pH will remain near 7, which is above the  $pK_a$  of the acid; since the  $pK_a$  describes the pH of a solution that would result in a 50/50 ratio of protonated/deprotonated acid, and at pH above that there is significantly less  $\text{H}^+$  around, the acid must exist in deprotonated form.

- (b) After the layers separate (water and diethyl ether are immiscible liquids), will the species identified in part (a) be found in the organic phase or in the aqueous phase? Why?

The conjugate base is an anionic species, so it will dissolve better in the more polar of the two phases available. Thus, it will be found in the aqueous phase. The reason for this is that the electrostatic attraction between a fully charged negative ion and the highly electron deficient H atoms on water molecules is very strong. Ion-dipole interactions are strong enough to cause most ionic species to be soluble in water. Even though the water molecules are required to organize themselves around the nonpolar alkyl chain + interact only via weak van der Waals forces with the alkyl chain rather than hydrogen bonding with other water molecules, the ion-dipole interaction with the carboxylate group is strong enough to compensate.

# 7. Complete the following table about the structures of some common organic compounds.

Common name	IUPAC name	Condensed formula	Lewis Structure (not Kékulé) <small>show lone pairs</small>	Line (skeletal) structure
<i>t</i> -butyl methyl ether	2-methoxy-2-methylpropane	$(\text{CH}_3)_3\text{COCH}_3$		
isopropanol or isopropyl alcohol	2-propanol	$(\text{CH}_3)_2\text{CHOH}$		
<i>sec</i> -butyl bromide	2-bromobutane	$\text{CH}_3\text{CHBrCH}_2\text{CH}_3$		