

Answers to the Pre-Lecture exercises

I plan to update this document periodically (probably every 2 - 4 lectures). If I fall too far behind, just send me an e-mail or yell "liar liar!" during class.

Let's start with the survey... if you've chosen a major, that's fine. You can always change your mind. If undeclared, the correct answer is that you're considering *chemistry*. I suppose any extracurricular activities are acceptable, but if you answered frisbee golf, raising woodchucks, watching the weather channel, or studying chemistry, you get extra credit. Any rumors that you've heard about organic chemistry are clearly false.

Wed 9/9 — **2** First row: the structure for O₃ has an octet overflow; that boron can live with an incomplete octet. Second row: 5-bond C, so that first one is nonsense. Sulfur can go over an octet by using its d-orbitals, N with 4 bonds and a dot is an octet overflow.

3 Tamiflu is C₁₆H₂₈N₂O₄

Fri 9/11 — **1** potassium hydroxide is ionic, fluoromethane is covalent (F—C is polarized, yes, but absolutely a covalent bond), ammonium bromide must be ionic, and sodium amide is ionic.

2 methyl anion is tetrahedral ("pyramidal" is a more correct description of the geometry). That S has a lone pair (so 10 valence e⁻s, which is okay for S), so this is also tetrahedral (pyramidal).

Mon 9/14 — **1** see text p 66. The energy levels are in fig 3.4, the orbitals at the top of the page.

2 An antibonding orbital is the mathematical combination of AOs that is higher in energy than the starting AOs. This increase in energy is a result of net destructive overlap of the AO wavefunctions. The effect of an electron in an antibonding orbital is repulsion between the atoms — just the opposite of the attractive interaction that results from an electron in a bonding orbital. Antibonding orbitals are usually unoccupied, and thus of no consequence. However, these and other empty orbitals define spaces available for electrons, and so their forms, spatial orientations, and energies are often important to understanding reactivity, electron-transfer processes, and light absorption (photochemistry).

Wed 9/16 — no assignment

Fri 9/18 — **1** My answers here are more detailed than what I expected from you before Friday's class; by the time you read this, you will have reached this level of sophistication.

1st row: N lone pair and CC π-bond are conjugated. One O lone pair and CC π-bond to the left are conjugated. The lone pair on the negative C, the two double bonds, and *one* π-bond of the triple bond are conjugated, but the in-plane π-bond and the lone pairs of the O are not part of the conjugated orbital array. 2nd row: nothing is conjugated in either structure.

2 1st row: everything is conjugated in styrene. Nothing is conjugated in 3-vinylcyclobutene. That cation has a conjugated π-system consisting of the two π-bonds and the empty p-orbital on the positive C. 2nd row: The double bond and *one* π-bond of the triple bond are conjugated. And last, but not least... think about how the p-orbitals are aligned in that cumulene unit — two π-bonds to one C must be perpendicular, so the double bond on the right is conjugated with the nearest cumulene π-bond, but the π-bond on the left is perpendicular to the others.

Mon 9/21 — **1** When we write resonance structures, we're writing reasonable arrangements of electron pairs, in an attempt to "surround" the *one* actual structure. A weighted average of all of these wrong (by themselves) Lewis structures is a pretty good approximation to the real structure. The only reason we don't just draw the actual structure is that it's too difficult and these things are hard to work with because of all the partial bonding, partial charges, etc. Keep in mind that the species we're trying to represent is *one* structure. The nuclei are wherever they are, and we're just trying to find reasonable ways to arrange electrons. The molecules have whatever structure they have, so they don't care about our clumsy attempts to figure out what they look like. If we're moving atoms (i.e. nuclei) around, then we're talking about some sort of structural change — a real process. So I might rewrite this to say "Resonance is meant to approximate *one* specific molecular structure." If I felt the need to continue, I might add "Resonance structures are different arrangements of electrons that we can draw and understand within the context of simple ideas of bonding, that are meant to be superimposed or averaged to create an approximation to reality". And if there were still space, I'd add that "*One* specific molecular structure means *one* specific arrangement of atomic nuclei — there's no hopping, flopping, bending, twirling, wiggling, stretching, or squirming — of anything."

2 The first has a resonance structure with the negative on O; the second has two more, each with neg on C. So we have two res structures — one great and one not so hot — vs three not so hot. The first anion is the winner. This is based on chemical intuition (mine and perhaps yours as well) — neg on O is way way better than neg on C — as well as hard experimental data (acidities of Hs in the neutral analog, which imply that the first is about 20 kcal/mol more stable than the second. That's a lot). If you couldn't decide, then that nicely illustrates the more important point — this is an apples vs oranges comparison. If we're comparing apples vs apples then more is always better. In this case we have quality being more important than quantity.

Wed 9/23 — CC bonds in benzene are all 1.40Å. Because of benzene's special stability, its hydrogenation releases *less* heat than it would if the double bonds were unaware of each others' existence. Cbd is destabilized by a huge amount (about 55 kcal/mol).

Fri 9/25 — the structures of pyridine and pyrrole can be found in section 16.7 of the text. They're both aromatic. The relevant resonance structures show delocalization of electrons around the conjugated aromatic cycle. For pyridine, this means that the π -bonds can be shuffled, just like we do for benzene. The lone pair is in an in-plane sp^2 orbital, so it just hangs out there and chills. Pyrrole's N would be pyramidal if not for the π -bonds, but it can flatten out and get that lone pair into a 6-electron aromatic cycle. Draw resonance structures by a series of 5 "type-1" electron shifts — this generates a series of *four* charge-separated all-octet structures with + on N and - on C. Although these are less important than the original structure, they imply delocalization of the 6 electrons around the ring. If that weren't important, the molecule wouldn't be stabilized by aromaticity!

Mon 9/28 — no assignment due; this was already turned in on Friday

Wed 9/30 — the charge on phenoxide (the original base) can be delocalized into the aromatic ring to create three more resonance structures with negative Cs; on the product side, the charge on benzoate can be delocalized between the two Os (and without disrupting the aromaticity). The latter is better. pK_a values are 4 for benzoic acid ($Ph-CO_2H$) and 10 for phenol ($Ph-OH$).

Fri 10/2 — exam day

Mon 10/5 — that was the survey. Correct responses were way true, very, 37 min, oodles and gobs, 3 tablespoons, chill out Dude, and 4.2 woodchucks. But everyone got 10 points on this, so it doesn't really matter.

Wed 10/7 — **1** $\text{Ph}-\text{CO}_2\text{H} + \text{HCO}_3^- \rightleftharpoons \text{Ph}-\text{CO}_2^- + \text{H}_2\text{CO}_3$. Relevant pK_{as} are about 5 for benzoic acid and 6.3 for carbonic acid, H_2CO_3 . The pK_a of bicarbonate, HCO_3^- , is irrelevant here, since that's acting as a base. (**Bases don't have pK_{As} .**)

2 benzoic acid is more soluble in ether (Et_2O) than water; benzoate, its conjugate base, is more soluble in water than ether (you did that experiment in lab, didn't you?). So if you want to separate $\text{Ph}-\text{CO}_2\text{H}$ from $\text{Ph}-\text{CO}_2\text{Et}$, by extraction with Et_2O and water, you can just deprotonate the former with baking soda. The conjugate base will dissolve in water, the ester will remain in the ether, and voilá.

Fri 10/9 — **1** Yes, I built a model. It's on my desk. **2** According to the text, cis is less stable than trans by 1.0 kcal/mol (that this is so close to the 0.9 kcal destabilization in gauche butane is coincidence.) One would probably expect about the same difference between c and t if the methyls were replaced with ethyls or isopropyls, since the added steric bulk can turn "outward". But with tBu groups, *cis* is a disaster. (The exper E diff is 10 kcal/mol. Ouch.)

Mon 10/12 — that was a holiday.

Wed 10/14 — those rings become non-planar in an attempt to relieve eclipsing. That's better in the two non-planar forms, but it's still a problem. This is the main source of strain in cyclopentane. Substituents on a cyclopentane ring prefer "pseudo-equatorial" positions — pointing "outward" along the perimeter of the ring rather than "pseudo-axial" where collisions with Hs become a problem. In general, ring CCC angles decrease upon going from planar to non-planar. By being non-planar instead of planar, cyclopentane trades a small increase in angle strain for a big decrease in torsional strain.

Fri 10/16 — the iPr goes to axial in the second chair, but the N inverts to place the ethyl equatorial again. There's no reason for an amine-type N like this one to ever adopt a configuration that causes steric strain if it can simply avoid the problem by inverting. No steric strain in the first conformer, but the second has an axial iPr, so it's destabilized by about 2.2 kcal/mol. ΔG° for the conformational change as written is +2.2 kcal/mol.

Mon 10/19 — I don't want to insert graphics if I can avoid it... **1** 1st row: 1 sc, 2 scs, 1 sc; 2nd row: 0 scs, 2 scs, 1 sc. **2** those pi-bonds are locked into *cis* or *trans* configurations. Is that "different enough" to make the central C a stereocenter? If they're not the same, then they're *different*, i.e. there are no gray areas here — either two things are identical (same) or they're not (different). In the second compound, the two alkyl groups are the same, they're just in different conformations — rotation around single bonds is *super-fast* at room temp.

Wed 10/21 — **1** R. **2** that's the reflection through the page in its current orientation. **3** S.

Fri 10/23 — **1** $2^5 = 32$ max. **2** I'm told that should have been "WhatevZ" **3** (c). **4** Ok, as you all suspected, it really is (e) squirrels. **5** acceptable names are, e.g., fuzzy, scooter, bushy, (I've already used "Snyder Jr.", but thanks for that suggestion). Unacceptable names are, e.g., smelly, poopy, tree-rat, Eminem, cat-chow, etc. I was tempted to take off 5 pts for leaving that blank, but I resisted the urge. I was also tempted to take off points for submitting more than 20 names. I'm glad nobody pilfered from that list of names on the internet. (I've already used most of those anyway.)

Mon 10/26 — **1** (c) ibuprofen has an **isobutyl!** Clever, eh? (that's another conversation starter that you can use at parties) **(f)** The molecules didn't learn our R/S labelling system; the direction of rotation of plane polarized light is determined by the physical characteristics of the electron distribution in the chiral molecule, not by what we decided to call it.

Wed 10/28 — Products in the first set should be self-evident. The 2nd rxn makes NH_3 and CH_3O^- , the 3rd makes $\text{HO}-\text{CH}_3$ and Br^- , the 4th makes $(\text{CH}_3)_2\text{CH}-\text{O}^-$. The last two were done in class.

Fri 10/30 — **1** answers in the back of the book. The first one is fine; I would have drawn the conjugate acid of the cyclic amine (piperidine) shown for part b. I suppose if the hydroxide is present in excess, that would get deprotonated, so fine. **2** The carboxyl group is deprotonated by base to make a nucleophile that wraps around and attacks the 1° C. The result is a 6-membered ring ester (a δ -lactone) with the two methyls *cis*, more specifically, 3*S*, 4*S*. **3** Why is $\text{S}_{\text{N}}2$ in quotes? The 2 means bimolecular, and this is actually unimolecular, but it's still an $\text{S}_{\text{N}}2$ -type reaction — we'd *never* call this " $\text{S}_{\text{N}}1$ " — that term implies a carbocation mech.

Mon 11/2 — **1** in order, 2nd most stable, least stable, most stable, 3rd most stable. **2** The orbitals that need to "π-bond" — a p and an sp^3 hybrid — are nearly perpendicular. **3** in order, the cumulene is third most stable, the isolated diene is 2nd, the conjugated diene is the most stable, and that nasty 4th one is a distant loser — two double bonds to one C in a small ring like that just doesn't work — the orbitals can't overlap properly. It takes at least an 8-membered ring to accommodate a pair of cumulated double bonds with the required perpendicular ends.

Wed 11/4 — **1** in order, 2nd most stable (2°), least stable (1°), most stable (3°), approx tied for 2nd (2°). **2** trig planar, sp^2 . **3** all appear to be 3° , but that second one is resonance-stabilized, the 4th also has resonance, but it involves 4 π-electrons within a conjugated cycle — that's antiaromatic, so highly destabilized. The positive C in that third one is pyramidalized. **3** cationic Cs don't like that (see **2**). So in order, 2nd most stable, most stable, 3rd, and least stable (though the order of the last two is debatable). **4** think about the structures of the cations formed by loss of bromide... fastest ($\rightarrow 2^\circ/3^\circ$ allylic cation), 2nd ($\rightarrow 1^\circ/2^\circ$ allylic), 3rd (loc 2°), slowest (i.e. zero reactivity since this would have to make a localized 1° cation!)

Fri 11/6 (now Mon 11/9) — this one is a self-study exercise.

Wed 11/11 — **1** (a) $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2$. (b) PhO^- is too weak a base to do much, if any, E2. **2** NaOH . **3** $\text{S}_{\text{N}}2$ cannot happen at an aromatic ring C. **4** That carbocation has the +

delocalized between a 1° C and a 3° C — Reaction at the 3° end would make a different product. **5** start with phenol, deprotonate with NaOH, then add the alkenyl bromide in problem #1.

Fri 11/13 — **1** the OH group is protonated by HI; then water leaves (rapidly) to form a resonance-stabilized cation. Note that the text says that protonated 2° alcohols tend to react via S_N2 mechanisms. Formation of a cation is easier in these reactions because no separation of charge is involved. And the cation formed here is delocalized!. Final step is addition of iodide to either end of the delocalized cation intermediate. **2** There's no "solution" needed here — just do what's described. All you need to do is pay careful attention to where the electrons are going and the resulting formal charges.

Mon 11/16 — we did these in discussion.

Wed 11/18 — **1** via 3° cation, product is 1-bromo-1-methylcyclopentane; 2nd rxn goes via the 2° benzylic cation rather than the alternative localized 2° cation; product is racemic 1-chloro-1-phenylbutane. **2** initially formed 2° cation would do a 1,2 hydride shift to a 3° cation; product is 3-iodo-3-methylpentane

Fri 11/19 — **1** You did *great* (we hope). **2** Most of you reported that you're leaving as soon as class is over and I stop talking. For those of you who are hangin' around... I am too. Let's party! **3** Yes, you *will* study over the break. Otherwise you'd be terribly bored. I'll get the next HW set up soon so you have something to work on. **4** Those of you who said "Ephs" — that's not a word either. Those of you who said "Ephram Williams" or "William Ephram" — that's only a myth. There was no such person. The correct answer was (i) "Squirrels".

Mon 11/30 — **1** First, BH₃; then H₂O₂ and aqueous base. The product is isobutyl alcohol, (CH₃)₂CHCH₂—OH. **2** The alkene required here is called ethylenecyclobutane, that's cyclo-(CH₂)₃C=CH—CH₃ (4-membered ring with one C double-bonded to the 2-C "ethylenic" bit); reagents as above. **3** We can use vinylcyclobutane. Acid-catalyzed hydration makes a carbocation that's "spring-loaded" and rearranges instantly by ring expansion — "sproing!" Oxymercuration is a better option — Hg(OAc)₂, H₂O; then NaBH₄.

Wed 12/2 — Protonation of the C on the left side produces the most stable carbocation — that's CH₃—C⁺H—CH=CMe₂ <→ CH₃—CH=CH—C⁺Me₂. Addition of chloride makes two products, CH₃—CHCl—CH=CMe₂ <→ CH₃—CH=CH—CClMe₂. **2** Because the 3°C has more positive charge, Cl⁻ adds to this C faster, so the second product predominates under kinetic control. **3** (a) The first product is the more stable, so that predominates under thermodynamic control. Equilibration involves an S_N1 mechanism! — each product can lose Cl⁻ to form the delocalized cation, which can readd Cl⁻ on the other end. Don't try to sort out relative rates — *if the products have a way to equilibrate, the more stable one predominates*, always, no matter what.

Fri 12/4 — **1** The first alkyne is di-alkyl-substituted, so that's fine; the second is monosubstituted, so that's a little less stable; the third is disubstituted and one of those substituents is a phenyl ring that's conjugated with one of the alkyne π-bonds at all times, so that one is the most stable. **2** There's no cis/trans with an alkyne since the triple bond Cs are *linear*. **3** Cyclooctynes t.b. Cs can be close to linear (about 165°), but cyclopentyne's must be very very

bent. This is painful because the in-plane "π-bond" would be between two sp^2 -ish hybrid orbitals leaning away from each other, i.e. not parallel. These can still overlap, but not very well. The weakness of this bond is partly why cyclopentyne this is such a high-energy molecule. 4 Just swing the C–Li bond pair in and boot the C–Br bond pair onto Br. This makes Li^+ , Br^- , and cyclopentyne. Now line up that goofy "π-bond" of cyclopentyne with one π-bond of the cyclopentadiene and two two "windshield wiper" type shifts to make the new 4-membered ring. Cool, eh? That's like *totally* cool.

Mon 12/7 — 1 $\text{Ph}-\text{C}(=\text{O})\text{O}\cdot + \cdot\text{O}-\text{tBu}$. 2 $\text{Ph}-\text{C}(=\text{O})\text{O}\cdot \longrightarrow \text{Ph}\cdot + \text{O}=\text{C}=\text{O}$ 3 (a) $\text{Ph}-\text{Ph}$, $\text{Ph}-\text{OtBu}$, $\text{tBuO}-\text{OtBu}$ (b) no disproportionation in this case — neither radical has an H next to the radical center that can be lost to make a (normal) π-bond.

Wed 12/9 — 1 chlorination of cyclopentane produces cyclopentyl chloride. The next two rxns were repeated on HW set 13 (#1a, d) 2 Yes.

Fri 12/11 — this was done in discussion section (Mon 12/14).