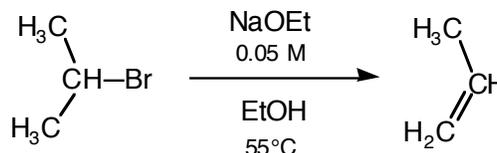# Chemistry 124   Fifth Examination Answers   **February 3, 2010**

Average score 79.5   1/3 > 85   2/3 > 77

1. (8 min) Influences on the rate of this elimination reaction:

A) Using $(CD_3)_2CHBr$ instead of *i*-PrBr slows the rate about 7-fold

B) Using of *i*-PrI instead of *i*-PrBr increases the rate

C)   Increasing [NaOEt] to 0.1 M doubles the rate

Consider the following five possible profiles for the reaction, four of which have a carbon cation or a carbon anion intermediate. Put an **X** in the box for each mechanism that **IS consistent** with each of the three observations above.

X

Mechanism		cation	anion	cation	anion
(A) D for H	X		X	X	
(B) I for Br	X	X		X	X
(C) 0.1M NaOEt	X		X	X	X

[Remember that changes that shift an initial, rapid eqilibrium toward the intermediate (*e.g.* I for Br with a cation intermediate, or increasing ethoxide with an anion intermediate) accelerate the reaction even when the second step is rate limiting (because they make the rate-determining transition state closer in energy to the starting material, or, which is the same thing, increase the concentration of "starting material" for the second step).]

2. (5 min) Explain the main logical error that was made when the structure of the ion illustrated on the right was used to "prove" that a trivalent carbon cation with two adjacent nucleophiles should be considered pentavalent.

That the distances O2-C19 and O1-C19 are shorter than C8-C9 and C1-C9, and that the C8-O2 and C1-O1 directions are bent in to shorten these distances, were taken to mean that there is an attractive interaction (bonding) between C19 and the flanking oxygen atoms, thus pentavalent carbon.
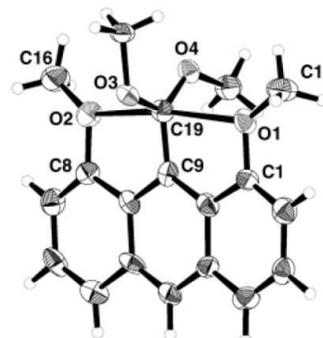
The error was to neglect repulsions between the methyl groups of C15 and C16 with the nearby hydrogen atoms on the aromatic rings. This repulsion moves O1 and O2 toward the center even more when there is a simple H atom in place of C19. There is no need of attraction toward the center to explain the positions of O1 and O2.

3. (5 min) **Draw three lines** to connect each radical in the second column with the corresponding dissociation energy (kcal/mole) in the first column for its bond to the H atom.

Then **explain the size of the other two** values relative to that for the H-CH_3 bond.

BDE $_{H-R}$	R
88.8	CH_3
105.0	$CH=CH_2$
110.7	CH_2-$CH=CH_2$

    The H-$CH=CH_2$ bond is unusually strong because it involves an sp^2 hybrid orbital on the vinyl group, which overlaps better that would an sp^3 hybrid. The starting material is unusually stable.

    The H-CH_2-$CH=CH_2$ bond is unusually weak because the allyl radical formed by its cleavage is resonance stabilized. That is, the new SOMO is able to overlap the π and π * orbitals of the C=C double bond, which results in lowering the energy of its π electrons.   The starting material is normal, but the product is unusually stable.

4. (2 min) Explain the source of the stabilization called "hydrogen bonding".

    H-bonding is due to elecgtrostatic dipole-dipole (or charge dipole) stabilization. It is much stronger than most dipole interactions, because these interactions are strongly distance dependant, and the H atom has such a small van der Waals radius that other dipoles or charges can approach it very closely.

5. (4 min) Why is cyclopropyl bromide so much slower to react in S_N2 substitution reactions than cyclopentyl bromide?

    The starting material is strained because the C-C-C bond angles that "want" to be ~109° are forced to be 60°. In the pentavalent transition state the carbon being attacked wants to have trigonal sp^2 hybridization for the bonds that are neither being formed nor broken, thus the transition state C-C-C bond angle is even more strained from 120° than the starting material bond of 109°. The increased strain in the transition state raises its relative energy and slows the reaction.

6. (4 min) List six factors that can be important in determining the pK_a for an organic acid (just name, no explanation)

A. Bond dissociation energy of the X-H bond (this includes overlap)

B. Energy mismatch between H and A (same as electronegativity, nuclear charge)

C. Resonance stabilization of the A⁻ anion.

D. Inductive electron withdrawal in the A⁻ anion.

E. Solvent stabilization (e.g. H-bonding) of H^+ and/or A⁻.

F.   Electrostatic change in the acid (e.g. H_3O^+ strong; ^-O_2C-CO_2H weak)

G. Field effect from a dipole within the molecule.

H. Polarizability of substituent groups or solvent.

[A number of answers included hyperconjugation, but this is not commonly a factor, since overlap with neighboring sigma bonds is a stabilizing factor for carbocations, but not for anions, unshared pairs, or O-H sigma bonds. One could imagine analogous stabilization by overlap of the anion HOMO with an adjacent C-halogen bond, but this would usually result in loss of the halide, giving an alkene by elimination.]

7. (6 min) Fill in the table by drawing two pairs of related acids with their pKa values (if you wish, one acid can appear in both pairs, in which case you would have a series of three acids, and explain below what their relative pKas teach about relevant factors you listed question 6.

PAIR I		PAIR II	
Structure	pK_a	Structure	pK_a
1		1	
2		2	
Lesson(s):		Lesson(s):	

This question is obviously too open-ended for a standard answer.

[It is worth noting that an extraordinary number of students chose to write about phosphorus-containing acids. I am deeply skeptical of some of the values in the Evans table, especially its dramatically different values for PH_4^+, $CH_3PH_3^+$, and Et_3PH^+. Note that in its other P-containing acids the proton is lost from an adjacent C atom, where the P encourages appearance of the carbon anion with an electron pair HOMO, because it supplies a vacant valence-level 3d AO that can overlap with it to give a resonance structure with a C=P double bond. This is especially favorable when the P atom bears a positive charge or is bonded to an electronegative O atom. The increased polarizability of the P atom (as compared to first-row elements) also helps stabilize the adjacent carbon anion.]

8. (2 min) Show the **principal product(s)** from the following reaction. (No mechanism necessary)

$$CH_3CH_2CH_2O^- + (CH_3)_3CCl \rightarrow CH_3CH_2CH_2OH + H_2C=C(CH_3)_2$$
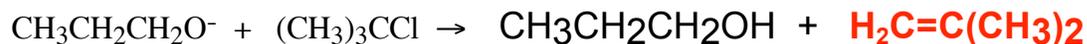
[A disappointing number of answers proposed S$_N$2 or S$_N$1 substitution.to give a propyl-*t*-butylether. S$_N$2 does not occur at hindered tertiary carbon centers, and with such a strong base to attack the proton, S$_N$1 should not compete effectively with E2 elimination. I am sorry we didn't drill on this more effectively, but at least we will have learned it now.]

9. (2 min) Show **reagent(s)** for accomplishing the following conversion in a practical manner. (No mechanism necessary).

$$(CH_3)_2CHCHOHCH_3 + PBr_3 \rightarrow (CH_3)_2CHCHBrCH_3$$

10. (3 min) What is done **to make radioactive fluoride a more reactive nucleophile**, so that a fluorinated analogue of glucose can be prepared rapidly for use in PET scanning.

H-bonding that stabilizes (deactivates) F$^-$ is eliminated by using an aprotic solvent (acetonitrile, CH$_3$CN), and by converting the OH groups of the sugar to acetate ester groups.
Stabilization of F$^-$ by the K$^+$ counterion is reduced by using a cryptand ligand to surround the K$^+$ and make it further from the F$^-$.

11. (3 min) Suppose you found that quadrupling the concentration of a reagent only doubles its reaction rate. How might this be explained?

This means that the reaction is ½ order in the reagent.

A common source of such dependance is that the dominant form of the reagent is dimeric, but the reactive form is monomeric. Doubling the concentration of the dimer increases the concentration of the monomer by a factor of the square root of 2.

We also discussed that free-radical-chain reactions are ½ order in the initiator, because the termination process is second order in radical concentration.

12. (6 min) C-H bond dissociation energies are often used to support the contention that more substituted free radicals are more stable (t-Bu > i-Pr > Et > CH$_3$ in stability). Explain briefly how other data casts doubt on this interpretation.

Although this order is observed for dissociation of R-H bonds, the analogous R-CH$_3$ bonds show less variation (and no significant variation if one corrects for steric strain in the starting material), while the analogous R-Cl and R-Br bonds trend in the opposite direction (after correction for starting material strain). Thus in the latter cases the trends cannot be explained by greater stability for more substituted radicals.