Kramer finds a way to spend more time studying organic:

From "The Friar’s Club"
Episode 128, Written by David Mandel

Kramer opens the door and leans in.

KRAMER: Knock on my door, wake me up in twenty minutes, alright?

JERRY: Catnap?

KRAMER: No, no, no, no. (comes in) This is evolutionary. I’ve been reading this book, on Leonardo da Vinci. See, that means ‘from Vinci’, d’you know that?

JERRY: (deadpan) That must be some book.

KRAMER: Yeah, well, turns out that the master slept only twenty minutes every three hours. Now, that works out to two and a half extra days, that I’m awake per week, every week. Which means, if I live to be eighty, I will have lived the equivalent of a hundred and five years.

JERRY: Just imagine how much more you’ll accomplish.

KRAMER: Oh, I got a lot of things in the hopper, buddy.

JERRY: I didn’t know you had a hopper.

KRAMER: (smiling) Oh, I’ve got a hopper. A big hopper.

Note: Your exam should consist of 5 pages including the cover page and grade tabulation sheet. Skim the entire exam and solve the easiest problems first. Exams not returned at the end of the period will not be graded.

PLEASE DO NOT OPEN THIS EXAM UNTIL YOU ARE INSTRUCTED TO DO SO.
1. Which product (or products) would you expect to obtain from each of the following reactions? In each part specify the mechanism (S_n1, S_n2, E1 or E2) by which the product is formed and predict the relative amount of each product (i.e., would the product be the only product, the major product, a minor product, etc.?) 20 pts

- t-Bu Cl Cl 2° \( \xrightarrow{\text{Nal, acetone, 50 °C}} \) H H

- Br 3° \( \xrightarrow{\text{MeOH, 25 °C}} \) MeO + racemic

- CH_3ONa 2° \( \xrightarrow{\text{CH_3OH, 50 °C}} \) major E2 minor Zaitsev

- Br 3° \( \xrightarrow{\text{EtOH, 55 °C}} \) OEt

Write the chemical structure(s) in the space provided and under each specify "major/minor" and "S_n1, S_n2, E1, or E2"

2. Circle the letter of the statement(s) that are true for reactions occurring by the S_n2 mechanism. 6 pts

a. Tertiary halides react faster than secondary.
b. The reaction shows first order kinetics.
c. The rate depends markedly on nucleophilicity.
d. The probable mechanism involves one concerted step.
e. Carboxations are intermediates.
f. The reaction rate is proportional to the concentration of the attacking nucleophile.

3. Compounds I and J both have molecular formula C_7H_{14}. Compounds I and J are both optically active and both rotate plane-polarized light in the same direction. On catalytic hydrogenation I and J yield the same compound K (C_7H_{18}). Compound K is optically active. Propose possible structures for I, J, and K. 6 pts

4. (S)-(3-Chloro-2-methylpropyl) methyl ether (A) on reaction with azide ion (N_3^-) in aqueous ethanol gives (R)-(3-azido-2-methylpropyl) methyl ether (B). Compound A has the structure ClCH_2CH(CH_3)CH_2OCH_3. (a) Draw wedge-dashed wedge-line formulas of A and B. (b) Is there a change in configuration during this reaction? Explain. 6 pts

No change of configuration occurs, just a change in the relative priority at the chirality center.
5. In class we discussed how a cis alkene can be isomerized to a trans alkene under conditions of 'partial hydrogenation' like that used in the food industry. Show how the hydrogenation reaction can produce the fully saturated product from a cis starting material and how the isomerized trans product can form. 10 pts

6. Match the listed heats of combustion with the following alkenes: cis-2-pentene, trans-2-pentene, 2-methyl-2-butene, 1-pentene. Write the structures in the boxes 8 pts

   a. 807.4 kcal/mol
   b. 806.0 kcal/mol
   c. 805.0 kcal/mol
   d. 802.6 kcal/mol

7. Propose a synthesis of tert-butyl methyl ether (TBME) using starting materials containing 4 or few carbon atoms. You may use any other needed reagents and you DO NOT need to show any mechanistic detail. 6 pts

8. Suggest an explanation for the following observations. Use annotated 3D structures to make your point. 12 pts

   A reacts faster by S_n2 than B
   C reacts slower by E2 than D

   Compound B has a more sterically hindered S_n2 trajectory because of axial Me group.
9. When methyl bromide is dissolved in methanol and an equimolar amount of sodium iodide is added, the concentration of the iodide ion quickly decreases, and then slowly returns to its original value. Explain, using lightly annotated chemical reactions. 6 pts

\[
\begin{align*}
\ce{I^+ + H_C-C-Br &<-> & I^- + H_C-C-Br^+} \\
\text{Mesh} & & \text{weaken bond} \\
\text{Good nuke in CH}_3\text{OH} & & \text{still good nuke in CH}_3\text{OH} \\
\text{OR: } & & \\
\ce{I^- - CH}_3 + \text{CH}_3\text{OH} &<-> & \text{CH}_3\text{OCH}_3 - I^- + \text{H}_2\text{O}
\end{align*}
\]

10. Propose an arrow-pushing mechanism to account for the following reaction (Note: D = deuterium, an isotope of hydrogen). 8 pts

\[
\begin{align*}
\text{Li metal (2 equiv.)} & & \\
\text{ND}_3 \text{ (liquid ammonia)} & -78 \degree C &
\end{align*}
\]

11. Carbocations bearing an oxygen atom are found to be exceptionally stable. Is this surprising to you? Use your knowledge of factors affecting carbocation stability to explain the origin of this stability. 6 pts

\[
\begin{align*}
\text{Surprising because } O \text{ is an electronegative atom - which should} \\
\text{inductively destabilize the cation:} \\
\text{Hyper-C Stabilization:} & \quad \text{a: inductive destabilization} \\
\text{Resonance Stabilization:} &
\end{align*}
\]

12. Propose an arrow-pushing mechanism to account for the reaction of B to C. 6 pts

\[
\begin{align*}
\ce{H_C-C-CH}_3 - \text{NH}_2 &<-> & \ce{H_C-C-CH}_3 + \text{N}_2(g) + \text{H}_2\text{O} \\
\text{HONO} & & \\
\text{B} & & \text{C}
\end{align*}
\]
Chemistry 110a
THIRD EXAM
October 17, 2014

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