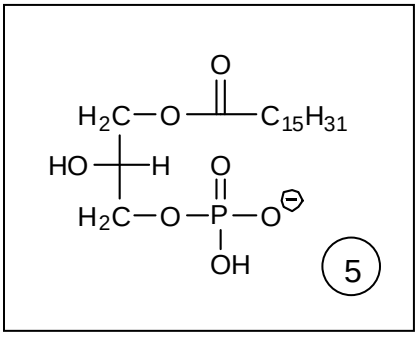
Chemistry 4361/8361 Monday, December 13, 2010

Exam 4
Answer Key

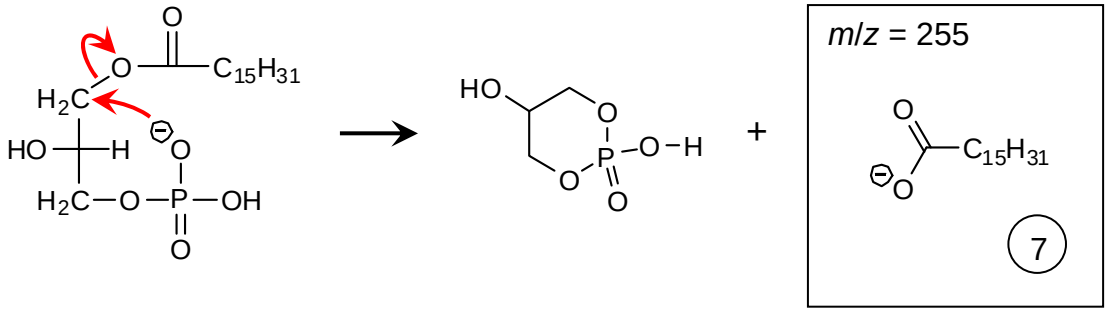
Exam 4 Mean:	65
Exam 4 Median:	65
Exam 4 St. Dev.:	18

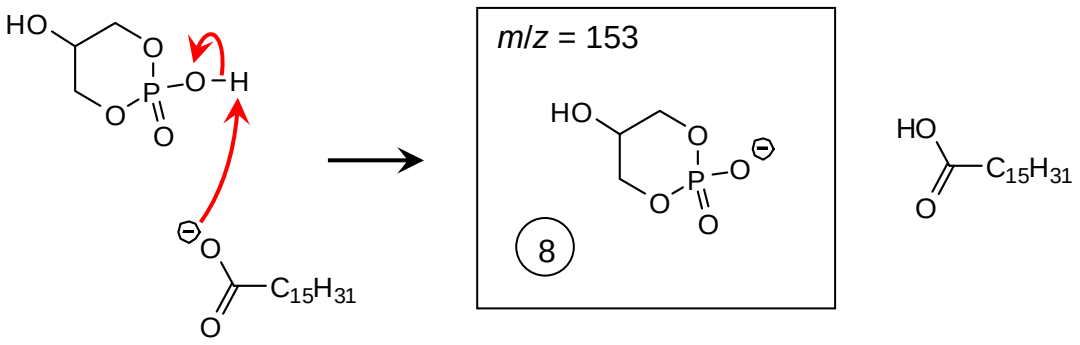
1. a. Because the method used here is negative-ion-mode ESI, the parent ion has to be a negatively charged ion, generated by deprotonating the neutral starting material to $[M-H]^-$. (Rather than protonating it to $[M+H]^+$, which is what happens in positive-ion-mode ESI.) The most acidic proton in the starting material is certainly one of the phosphate/phosphoric acid protons, so that's the one I propose.



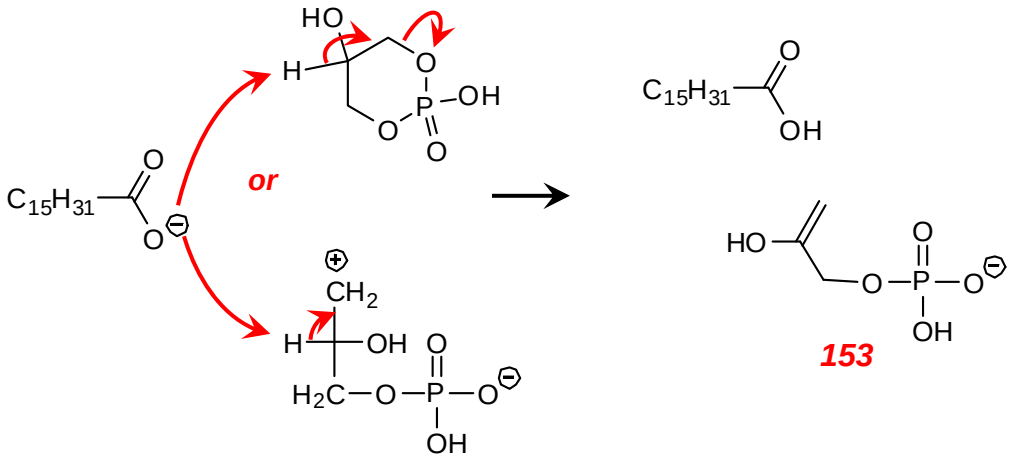
Rubric:
5 points for correct anion.
4 points partial for deprotonating alcohol instead.
No partial for a (protonated) cation.

b. The alkyl ($-C_{15}H_{31}$) group, all by itself, has mass 211. I haven't given you any structure for this part of the molecule, and alkyl groups don't tend to split in half spontaneously anyway, so it's likely this part will stay intact. That means it must be part of the *m*/*z* = 255 ion, and it must not be a part of the *m*/*z* = 153 ion.





There are actually a few possible answers for the *m*/*z* = 153 fragment, based on what we spoke about in class. We said that β-elimination was a common fragmentation mechanism in ESI, and that could certainly happen here:



I don't think this is as likely as the answer I gave, given how much more acidic a phosphoric acid proton will be compared to an alkyl hydrogen, but it could still happen. Or alternately, the phosphate group could remain protonated, and the proton could come from the alcohol--again unlikely given the pK_a of an alcohol relative to phosphoric acid.

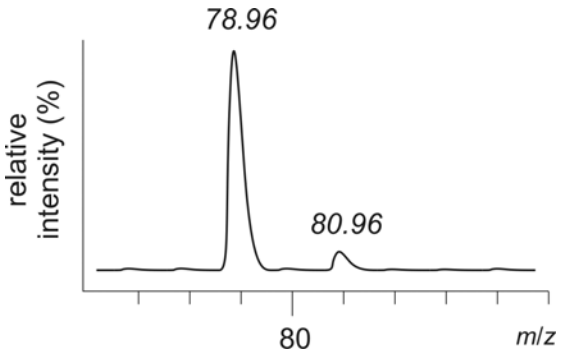
Rubric:

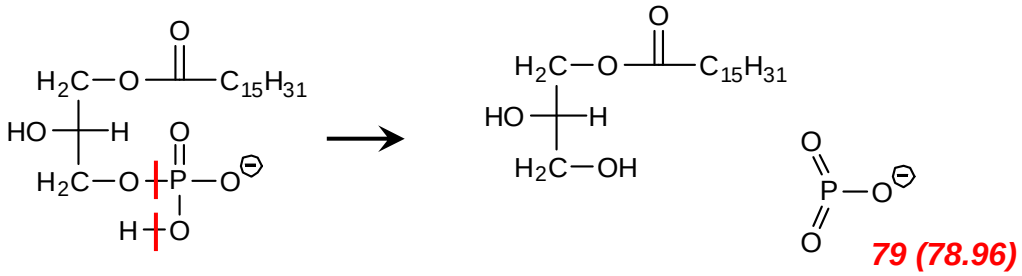
7 points for carboxylate. *No partial credit.*

8 points for glycerol/phosphate anion.

- *7 points partial for elimination product (w/ alkene).*
- *6 points partial for alkene or correct answer, but with alcohol deprotonated instead of phosphate.*
- *3 points partial for any answer with correct mass, but with a cation (say, at terminal -CH_2). To observe in negative ion mode, you would also need two anions, and that's be tough to do in one molecule.*

c. In order to answer this part of this problem, you needed to figure out what the *m*/*z* = 79 fragment is. If you didn't already know what it was, the mass labels in the mass spectrum give a hint; they show that the fragment has a negative mass defect, which must come not from C or H (both positive mass defect), but from P and/or O (both negative mass defect). The only way to get near *m*/*z* = 79 using P's and O's is PO_3^-.





This will actually make our calculation easy--all we need to do is determine [A+1] and [A+2] probabilities for P and O. Phosphorus only has one stable isotope, ^{31}P, so it contributes nothing to I_{80} or I_{81}. Oxygen, on the other hand, has both ^{17}O and ^{18}O isotopes in addition to the predominant ^{16}O isotope. Calculating probabilities,

Probability of [A+1] relative to [A]:

^{17}O: I_{80} = 0.038% x 3 = **0.11%** (6)

Probability of [A+2] relative to [A]:

^{18}O: I_{81} = 0.205% x 3 = **0.62%** (6)

Rubric:
6 points each box.
Must be within 0.2%.
So [A+1] could be 0%-0.31%, and [A+2] could be 0.42%-0.82%.

Technically speaking, the values should be a tiny bit smaller than this, because I haven't removed the probability that the ion has two or three ^{17}O's/^{18}O's. That probability is extremely small though, so I think my values are very close.

d.

One problem with the lipid structure I gave you is that "$C_{15}H_{31}$" is not very descriptive. Sure, it indicates that the C_{15} alkyl group is saturated, but is it completely linear, or is it branched? If branched, where?

I think this easiest way to get this information from mass spectrometry is to perform a tandem MS (MS-MS, or MS^2) experiment. The experiment described in the problem already generates fragment ions with *m*/*z* = 255, corresponding to the C_{15} ester group. In an MS-MS experiment, these *m*/*z* = 255 ions would be mass-selected in a first quadrupole, and then accelerated into a collision-induced dissociation (CID) chamber filled with collision gas to induce further fragmentation. The resulting fragment ions would be mass-analyzed by a second quadrupole. In principle, the pattern of fragment ions from the CID experiment could say something about whether the alkyl group was branched, and where along the chain the branch was. (See Workshop 6 for an example of what this analysis might look like.)

(18) *total.*

Rubric:

7 points for "Tandem MS", "MS-MS", or "MS^2", or for describing a double-selection experiment that essentially is a tandem MS experiment.

7 points for explicitly naming *m*/*z* = 255 ion as a target of selection.

Just saying that you'll select an ion is not enough. This is part of any Tandem MS experiment, so the first 7 points rewarded you for this already.

4 points for stating that collisional fragmentation (or "CID" is enough) of this ion would give information on structure.

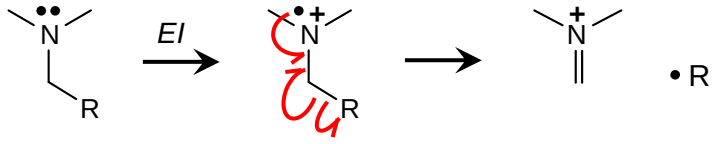
2. a. Our molecule has a chemical formula of **$C_6H_{15}N$**, and that means it has a degree of unsaturation of

$$UN = \#C - \frac{\#H}{2} - \frac{\#Hal}{2} + \frac{\#N}{2} + 1$$

$$= 6 - 7\tfrac{1}{2} - 0 + \tfrac{1}{2} + 1 = \mathbf{0}.$$

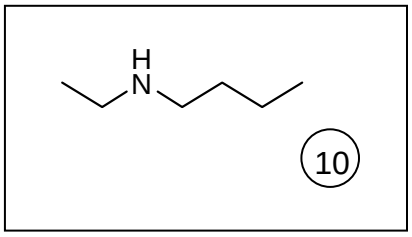
This means our molecule has no rings and no multiple bonds in it—it has to be an alkylated amine.

Amines have one lone pair, which will be preferentially ionized. The resulting radical cation should cleave much like an alcohol or ether does. One extremely important fragmentation pathway we highlighted in class for lone-pair-bearing atoms in EI is α-cleavage:



(The section of Pretsch that deals with EI fragmentation of amines calls this "N-fragmentation".) It seems likely that at least one of the fragments should come from this fragmentation pathway. The *m/z* = 86 (loss of 15, •CH_3) and *m/z* = 58 (loss of 43, •$CH_2CH_2CH_3$) peaks might be attributed to α-cleavage, but I don't think the *m/z* = 30 peak can be.

We gave almost full credit to any answer that could do the α-cleavage fragmentation. I think that to make the *m/z* = 30 fragment, the molecule has to be a secondary amine with at least one -CH_2- unit adjacent. (I'll explain that below.)



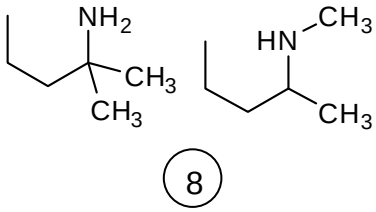
Rubric:

10 points for correct structure.

-4 points for structure that does not have formula $C_6H_{15}N$.

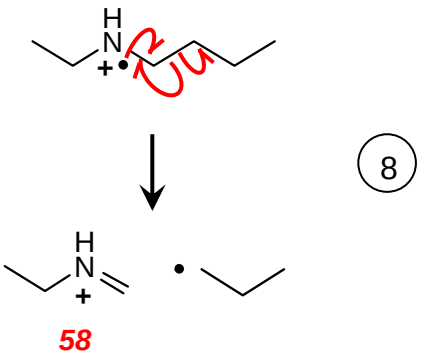
8 points partial for any $C_6H_{15}N$ structure that could generate both m/z = 86 and m/z = 58 by α-cleavage. (4 points partial if not $C_6H_{15}N$.)

6 points partial for any $C_6H_{15}N$ structure that could only generate one of two α-cleavage fragments. (2 points partial if not $C_6H_{15}N$.)



b. For this problem, you did NOT have to have the correct answer to part (a). You did, however, need to draw a reasonable radical mechanism to the indicated fragment.

mechanism for *m*/*z* = 58 fragment

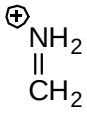


Rubric:

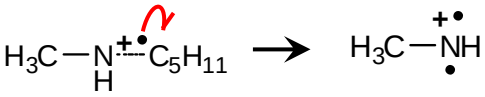
6 points for any α-cleavage mechanism.
- *2 points partial for each single-headed arrow.*
- *-1 point for each error in valency, charge or bonding.*

2 points for drawing any product ion with *m* = 58.

mechanism for *m*/*z* = 30 fragment

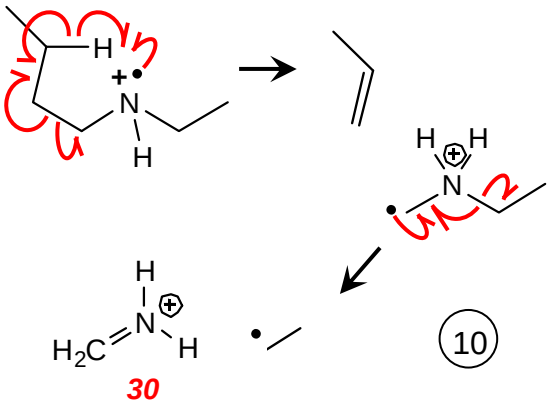
Fragment structure must be  ;

no other way to arrange electrons, C's, H's and N's to make reasonable cation or radical cation. (Can't do



charge would prefer carbon.)

Only way to get to this fragment is to transfer H to secondary N:



You might also be able to draw this in a single step.

Rubric:

4 points for drawing correct product ion with *m* = 30.

6 points for mechanism; grader's choice.
- *-1 points for each unreasonable single-headed arrow.*
- *-1 point for each error in valency, charge or bonding.*

c. If the mass spectrum of this unknown were obtained via atmospheric pressure photoionization (APPI) instead of EI, would there be

more or **less** or **the same amount of** fragmentation? (Circle one.)

5

What would the parent ion *m*/*z* be in this case? **101** 6

APPI is a mild ionization technique that removes an electron from the molecule by exciting it to the vacuum level (the energy required to eliminate any attraction of the electron for the molecule) with a photon. Very little fragmentation occurs because no excess energy is transferred, and the parent mass is the same as the molecular mass.

d. If the mass spectrum of this unknown were obtained via chemical ionization (CI) using CH_4 as the reagent gas instead of via EI, would there be

more or **less** or **the same amount of** fragmentation? (Circle one.)

5

What would the parent ion *m*/*z* be in this case? **102** 6

CI with CH_4 involves the intermediate generation of CH_5^+ by EI. CH_5^+ is a very strong acid, and will protonate just about anything with electrons to give. In this case, the resulting parent would be the protonated ammonium ion $[M+H]^+$. However, CI generally produces less fragmentation than EI.