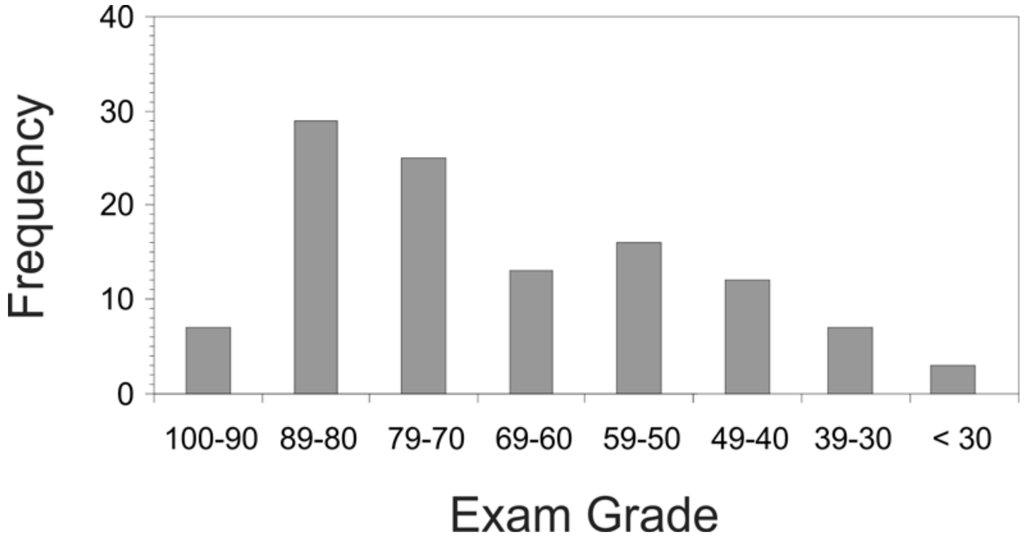
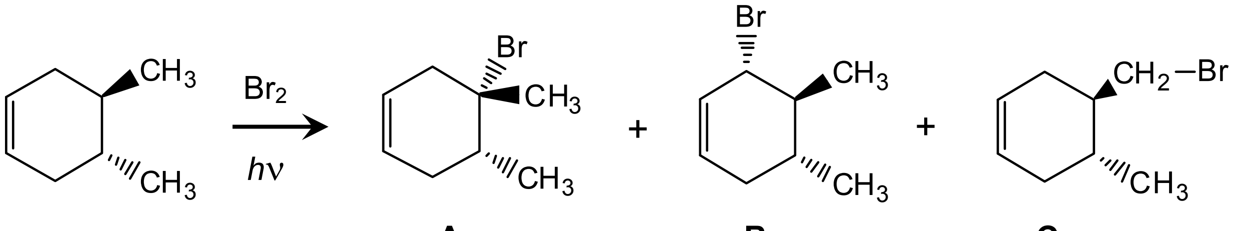
Chemistry 2301 Wednesday, August 6, 2014

# Exam 4
# Answer Key

Exam 4 Mean: 67
Exam 4 Median: 71
Exam 4 St. Dev.: 18

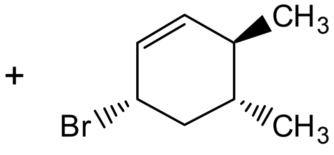


1. (35 pts) When the starting material below is exposed to the conditions of free-radical bromination, four monobrominated products (**A**-**D**) are isolated.



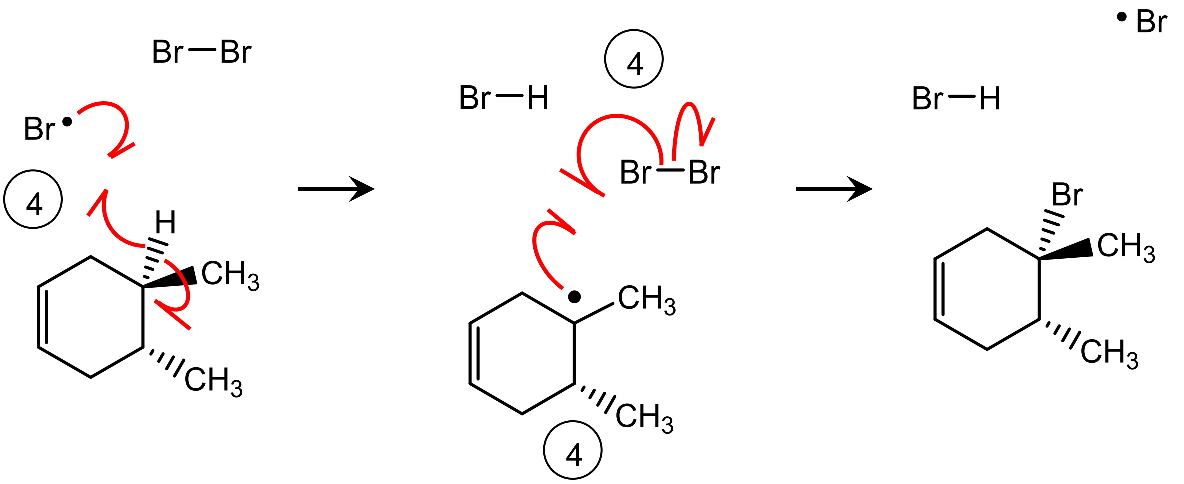
**A** **B** **C**

a. In the box below, draw a mechanism of **two propagation steps** that explains how product **A** would be made from a combination of starting material, $Br_2$, and Br• radical. *Because you have been supplied with Br•, you do* *<u>not</u>* *need to draw an initiation step.*



**D**

*Mechanism:*



<u>Rubric for this part:</u> *(12 points total)*

Overall notes:

4 points for each electron-pushing step. (8 points total from two steps.)

*Overall, the minimum score for each step is zero; errors in a step cannot earn you negative points that count against another, correct step.*

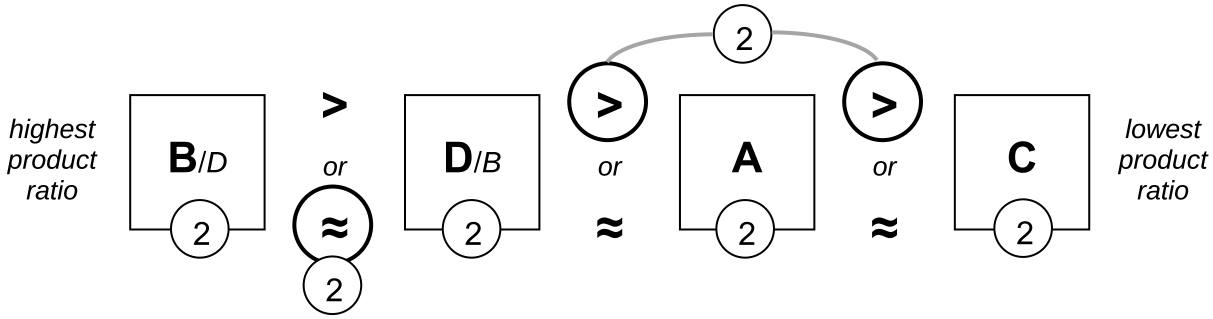
*-2 points, for each arrow in each step, for errors (including omission) in drawing arrows. Each arrow in this problem must be *single-barbed*. Double-barbed arrows earn no partial credit. Arrow must start at an unpaired electron or an electron pair, and end at a nucleus or newly formed bond.*

4 points for radical intermediate.

*Things that have left (e.g., HBr produced in first step) may be omitted. Only organic things that change need to be drawn.*

*-2 points for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.*

b. How would the four molecules **A**-**D** relate in terms of product ratio? Which product would be most prevalent, and which would be least prevalent? In the boxes below, rank the four molecules (by letter) from highest to lowest product ratio. If any two molecules would be observed at equal ratios, circle the "≈" sign between those two boxes.



Rubric (12 points total):

2 points for each box.

*No partial credit. Each box is graded individually.*

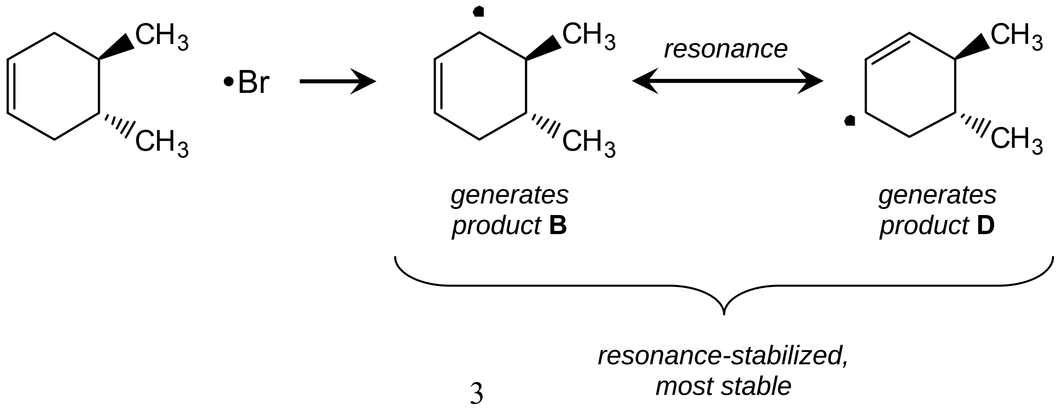
*First two boxes can be either B or D (order doesn't matter).*

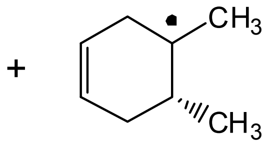
2 points for saying B and D are equal.

*You get these points regardless of where B and D are in sequence. For example,* C > A > D ≈ B *gets these 2 points.*

2 points for not having any other equal signs circled.

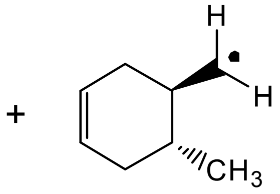
The selectivity of this radical halogenation will be determined by the stability of the intermediate radical produced. An allylic radical is the most stable radical that can be made here, followed by a tertiary radical, and then a primary radical. This is backed up by the bond dissociation energy (BDE) table, which shows an allylic C-H bond is weakest, followed by a tertiary C-H bond and then a primary C-H bond.





*generates product* **C**

*tertiary, but not resonance-stabilized*

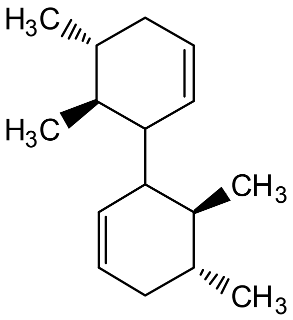


*generates product* **A**

*primary—least stable*

c. The free-radical chain reaction that generates products **A**-**D** is slowed by <u>termination</u> reactions that remove radicals from the reaction cycle. In the box on the right, draw one termination product that would be observed for the reaction above, *other than* $Br_2$ *and products* **A**-**D**. (So, do <u>not</u> draw $Br_2$ or any of the products **A**-**D** above as an answer to this part.)

*a termination product* ④



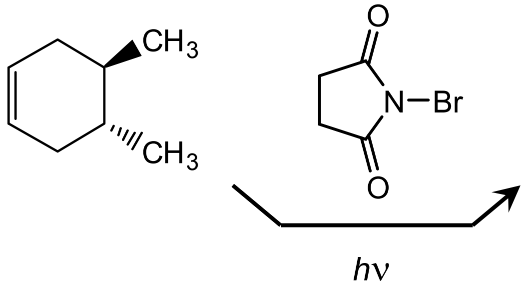
Termination is the process by which two radicals in the free-radical chain reaction combine to form a stable product. (We described it as step "4" in lecture.) That can involve combination of any two of the radicals above.

<u>Rubric:</u>
4 points for any combination of any of the radicals above (homo- or hetero-dimer).
*-2 points for each clearly trivial structure mistake.*

d. If the reaction on the previous page were a chlorination instead of a bromination—using $Cl_2$ instead of $Br_2$—would your preferred product be made

**more selectively** , [✓ **less selectively**] ③ , *or* **with the same selectivity** ?

e. If the starting material is halogenated with *N*-bromosuccinimide instead of $Br_2$, only two of the four products **A**-**D** would be formed. Which two?



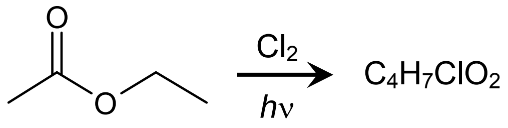
**A** , [✓ **B**] ② , **C** *or* [✓ **D**] ②

*(Circle two answers.)*

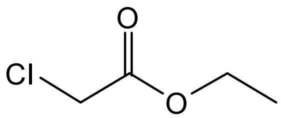
*N*-bromosuccinimide will only brominate allylic C-H bonds, via the allylic radical shown on the previous page.

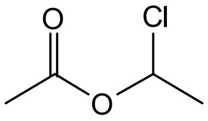
<u>Rubric:</u>
2 points for each correct circled answer.
*-2 points for each incorrect circle above 2. So if you circled 3 answers, -2; if you circled all 4 answers, -4 (so total 0 points).*

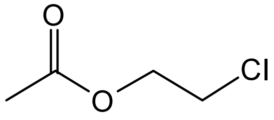
2. (65 pts) Radical chlorination of ethyl acetate ($C_4H_8O_2$, the starting material on the right) gives predominantly one product. This product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the following pages. High-resolution mass spectrometry determined an exact mass of 122.0135 amu for one of the highest-mass (parent, $\mathbf{M^+}$) peaks in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_4H_7ClO_2}$.



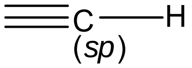
Before you even answered any of the parts of this problem, you already had a great deal of information about what was going on. The starting material has molecular formula $C_4H_8O_2$, so this reaction replaces an H with a Cl. That makes a lot of sense, considering that the reaction conditions are for radical chlorination, and this reaction normally replaces an H with a Cl. However, we don't know anything about the selectivity of radical chlorination of esters, and the molecule could even rearrange under these conditions to form something other than an ester. Nevertheless, if we assume that things don't change dramatically, we might be looking at simple replacement product candidates like

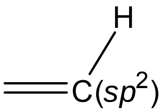


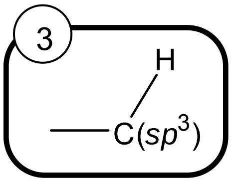


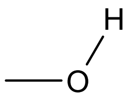


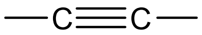
a. Based on the two peaks labeled in the IR spectrum below, what functional groups would you expect the unknown molecule to have? **Circle all answers that apply.**

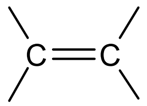


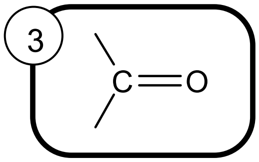










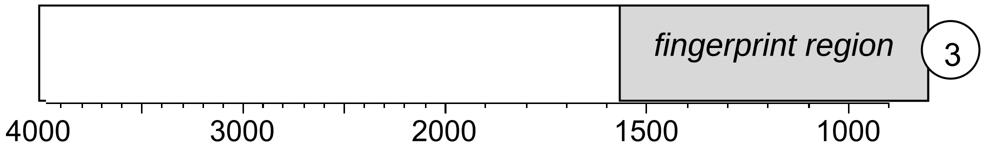


Rubric for part (a):

3 points for each correct circle.

*-3 for each incorrect circle (up to 2; minimum score for this part is zero).*

b. What part of this IR spectrum is the “fingerprint region”? In the box below, color/shade in the range of frequencies that correspond to the “fingerprint region”.



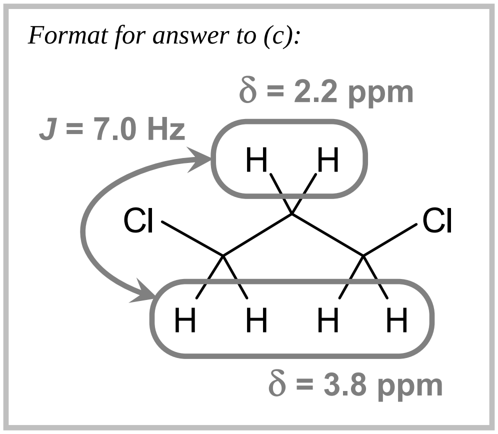
for anything close

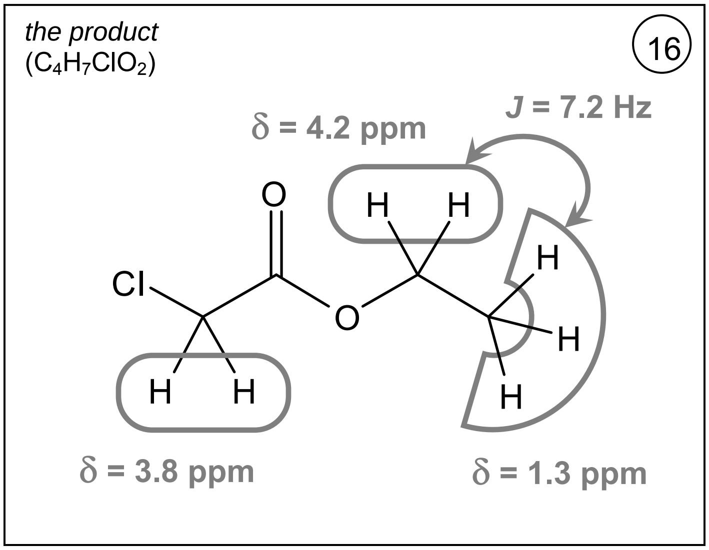
c. Compared to NMR, does IR require **MORE** *or* [✓ **LESS**] material? ③

d. Compared to mass spec, does IR require [✓ **MORE**] *or* **LESS** material? ③

e. **What is the structure of the product**? In the box below, draw the molecule's structure, including all hydrogens. Then, considering the $^1$H NMR spectrum below,

- Circle each group of equivalent H's;
- Assign a $^1$H chemical shift (δ) to each circled group, within 0.1 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).





Rubric for part (e):

*Structure need not be correct to receive points in this problem.*

4 points for the correct molecule.

3 points for assigning each δ value. (9 points total.) To get 3 points, circle must include all equivalent protons for your structure, match the integration intensity of the peak, and match the type of proton that would appear at that frequency.

*4.2, 3.8 ppm:* Must be $CH_n$ protons adjacent to an electronegative atom (O, Cl, or both).

*2 points partial for assigning each ppm value to the wrong number of H's, or with the wrong number of neighbors. If multiple inequivalent H's are labeled with the same δ value, you get maximum 2 point partial credit for each δ value.*

*1.3 ppm:* One lone alkyl methyl group.

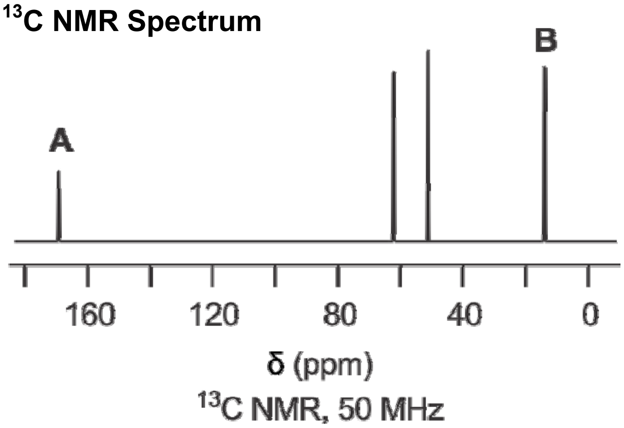
*2 points partial if methyl group has neighboring H's.*

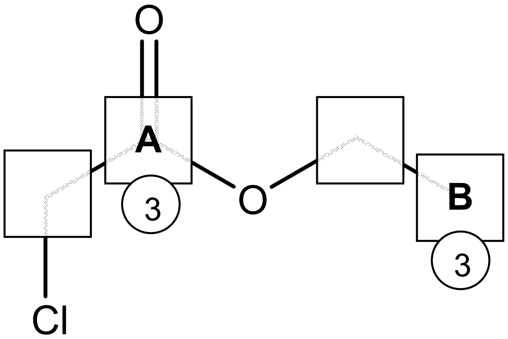
3 points for *J* assignment.

*Circles need not be correct to get these points, but shift assignments of coupled protons must be. Curved arrow only needs to connect one proton with an adjacent partner.*

f. The $^{13}C$ NMR spectrum of the product is shown below, with two peaks labeled **A** and **B**. Which carbons in the product do these peaks correspond to? On the unfinished molecular skeleton on the right, draw the chlorine atom that I've omitted from the product. Then, write the letters "**A**" and "**B**" in the boxes of the carbon atoms that are responsible for the two labeled peaks. *Leave two of the boxes empty.*

**$^{13}C$ NMR Spectrum**





Rubric for part (f):
*Structure need not be correct to receive points in this problem.*
3 points for **A** assigned to carbonyl carbon.
3 points for **B** assigned to any carbon with no attached O or Cl atom.

g. Some of the peaks in the electron-ionization (EI) mass spectrum (shown above), including the parent peak, are accompanied by a smaller peak that is 2 atomic mass units (amu) higher in mass. (In other words, some peaks with mass *m* are accompanied by another peak, about 1/3 as tall, with mass *m*+2.) Why? *Please be brief; you can probably answer this question in less than 10 words.*

*Explain why:* ④

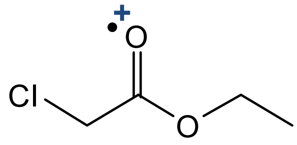
All of these pairs of peaks represent ions that contain one chlorine atom. Because chlorine has two common isotopes—$^{35}Cl$ (75% abundance) and $^{37}Cl$ (25% abundance)—every ion that contains chlorine shows up as a pair of peaks at mass *m* and *m*+2.

Rubric for part (g):
4 points for the words "chlorine" and "isotopes" in your answer.
*2 points partial for just isotope or chlorine.*

h. The parent mass peak at *m*/*z* = 122 corresponds to a radical cation (**M**$^{\bullet +}$) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw **M**$^{\bullet +}$; re-draw the structure you drew in part (e), but specifically indicate which electron is removed by drawing the molecule with one less electron. *Feel free to omit the hydrogens you drew in part (e).*

***M***$^{\bullet +}$
($C_4H_7ClO_2^{+}$)

④



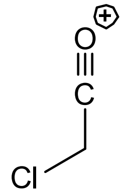
Rubric for part (h):

*Structure need not be correct to receive points in this problem.*

4 points for any molecule that (i) has formula $C_4H_7ClO_2$ and (ii) has a lone-pair electron on oxygen or chlorine removed (leaving a radical cation).

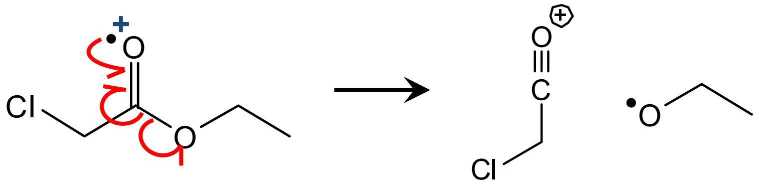
i. The parent ion fragments to form a daughter ion with m/z = 77. What is the structure of this daughter ion? *You do not need to do electron pushing to answer this part—just draw the cation.*

*fragment cation with m/z = 77*



④

This ion comes from cleavage of the ester C-O bond:



Rubric for part (i):

*Structures need not be correct to receive points in this problem.*

4 points for correct answer.

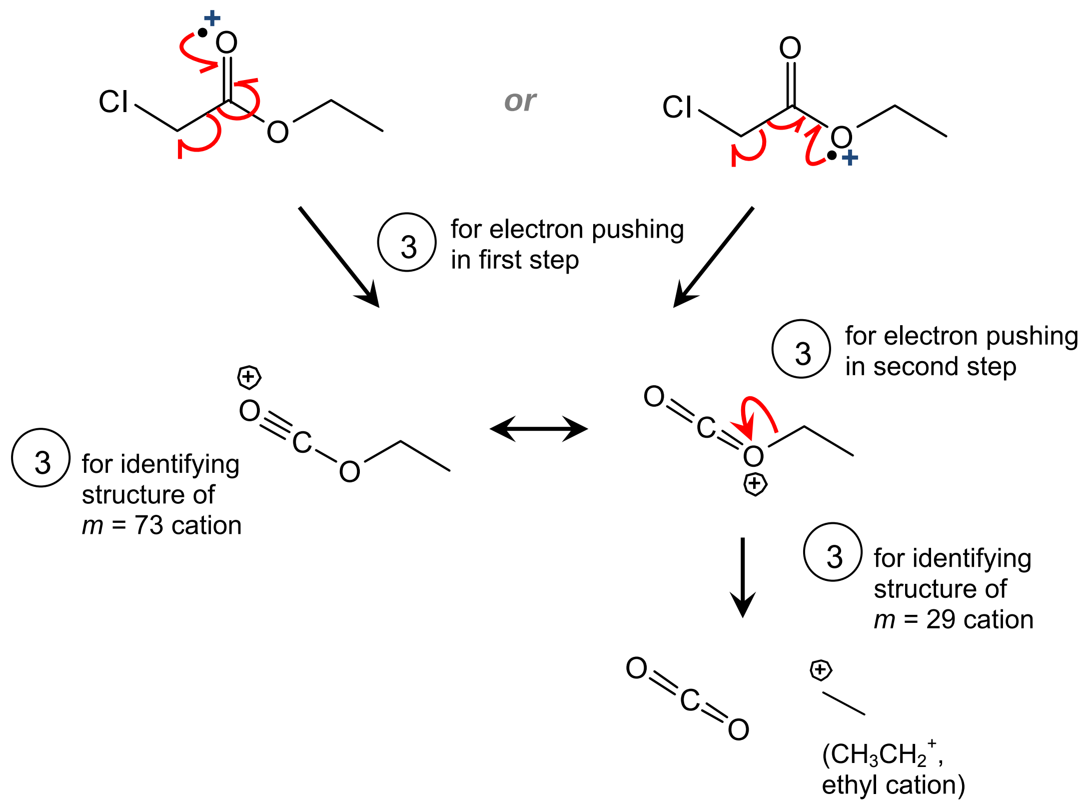
*-or-*

4 points for any fragments that are substructures of answer to (b), that have the right mass, and that are drawn as cations.

*-2 points for omitting positive charge.*

j. The parent ion also fragments to form a daughter ion with mass 73 amu (not observed), which then fragments further to give an ion with m/z = 29. In the box below, draw a mechanism (using "arrow pushing") that shows these two sequential fragmentation steps, starting with your answer to part (h).

*Mechanism that explains m/z = 29 peak*



Rubric for part (j):

3 points for each electron-pushing step. (6 points total from two steps.)

*In order to earn these points, the electron pushing needs to make sense, both in terms of the mechanism and in terms of the starting ion.*

3 points for identifying each correct cation structure.

*The mechanism does not have to be correct to receive these points.*

**+ AUTOMATIC 4 POINTS** because I messed up the math for this problem.