Student ID Number:

Total Score

/ 200

Chem 30B Spring 2004

FINAL
(180 Min)

Tues June 15th

Course Grade

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO

*ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED*

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM –
DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

Q1	/ 30	Q6	/ 18	Q11 BONUS	/ 14
Q2	/ 20	Q7	/ 18	Q12 BONUS	/ 12
Q3	/ 25	Q8	/ 9	Q13 BONUS	/ 4
Q4	/ 20	Q9	/ 10	Total	/ 200
Q5	/ 14	Q10	/ 36	Final Course Grade	

"It is possible to store the mind with a million facts and still be entirely uneducated." — Alec Bourne

"An education isn't how much you have committed to memory, or even how much you know. It's being able to differentiate between what you do know and what you don't." — Anatole France

Question 1. Compound **A** can be converted into either compound **B**, **C**, or **D**, depending upon what reagents are chosen, i.e., **E**, **F**, and **G**, respectively. Using the characterization data (1H-NMR, 13C-NMR, IR spectroscopies and mass spectrometry) shown below for each compound, propose structures for compounds **A**, **B**, **C**, and **D**, (6 points each) and the appropriate reagents **E**, **F**, and **G**, (2 points each) to achieve the transformation of **A** into each of **B**, **C**, and **D**, respectively. (30 points)
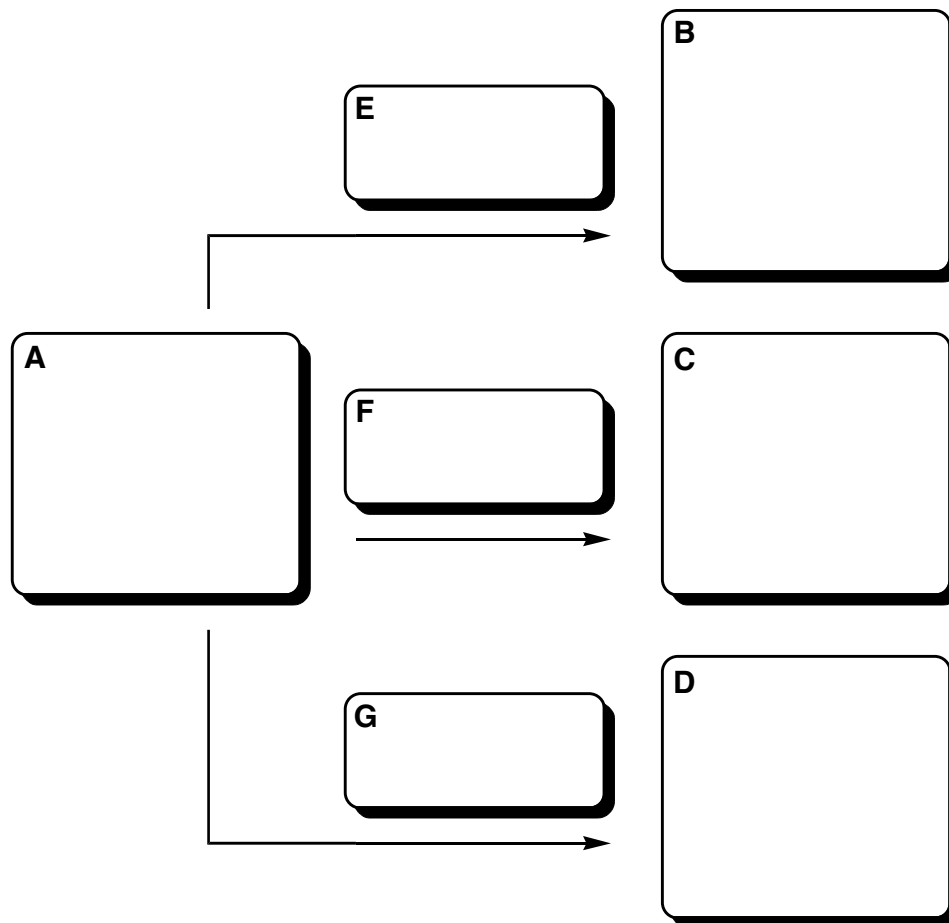
Cmpd **A**   MS: $m/z = 69$
1H-NMR: δ = 1.33 (doublet, 6H), 2.72 (septet, 1H)
13C-NMR: δ = 19, 20, 124

Cmpd **B**   MS: $m/z = 73$
1H-NMR: δ = 1.28 (doublet, 6H), 1.50 (broad singlet, 2H), 2.87 (nonet, 1H), 3.82 (doublet, 2H)
13C-NMR: δ = 20, 32, 50

Cmpd **C**   MS: $m/z = 88$
1H-NMR: δ = 1.20 (doublet, 6H), 2.58 (septet, 1H), 11.88 (broad singlet, 1H)
13C-NMR: δ = 19, 34, 184
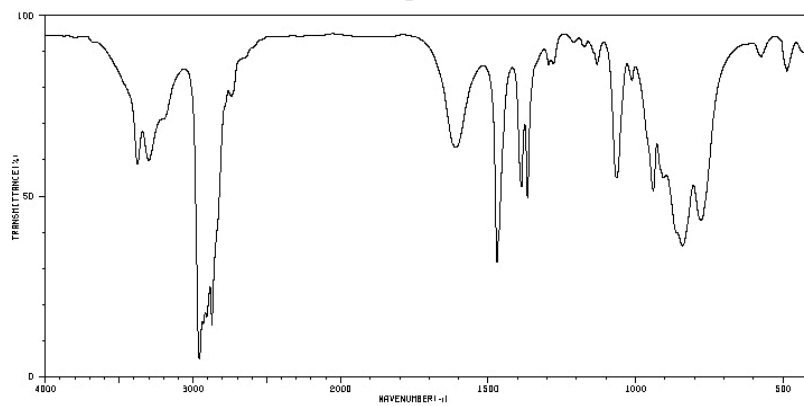
Cmpd **D**   MS: $m/z = 72$
1H-NMR: δ = 1.06 (doublet, 6H), 2.39 (septet, 1H), 9.57 (singlet, 1H)
13C-NMR: δ = 15, 41, 205

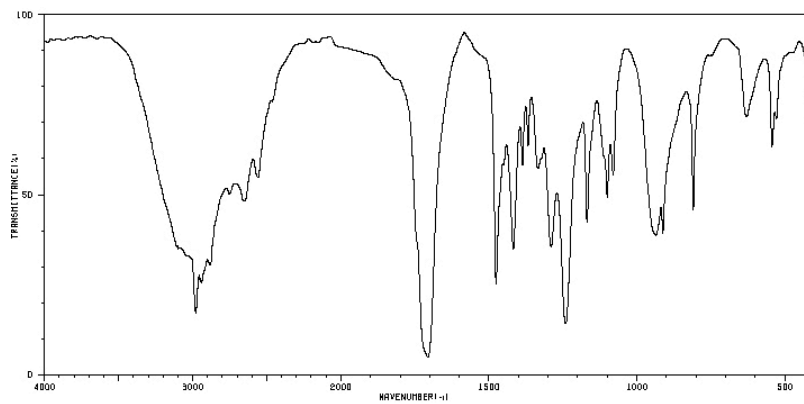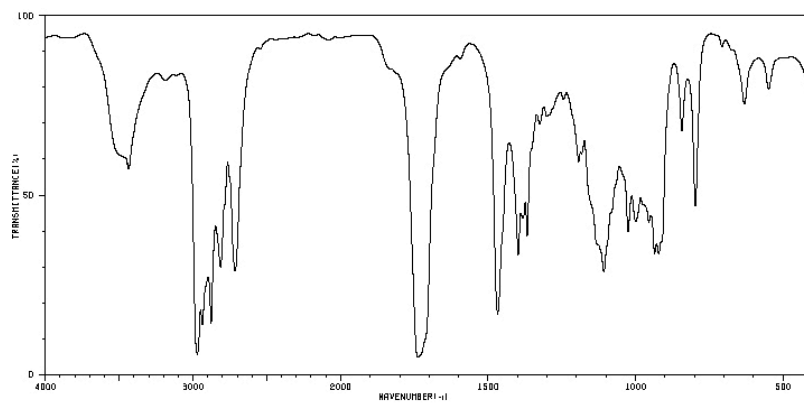*For ease of comparison, all of the IR spectra are lined up on the next page –*

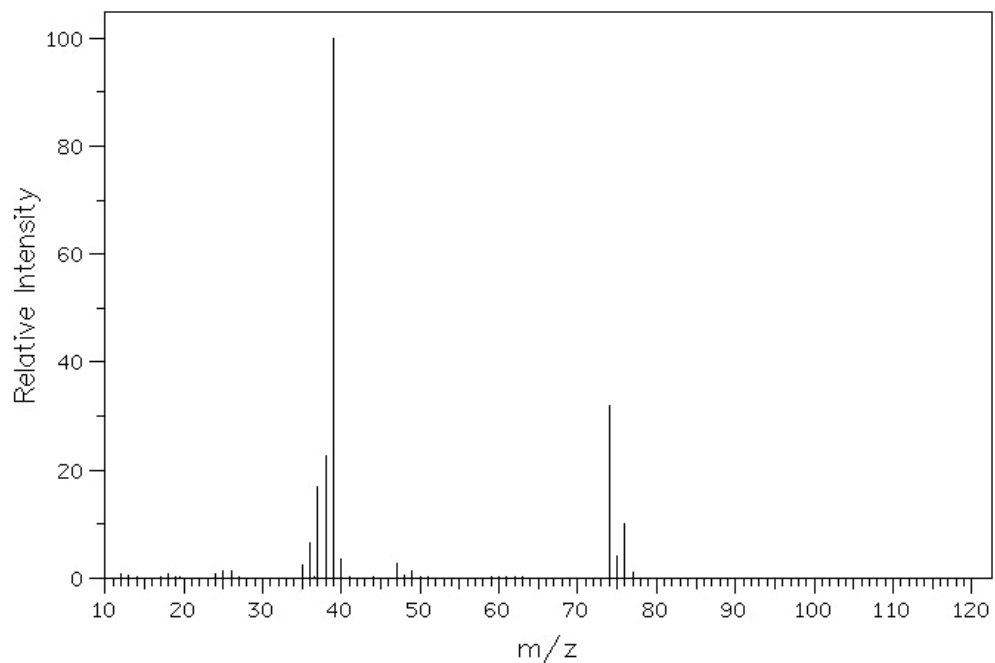## Cmpd **A**
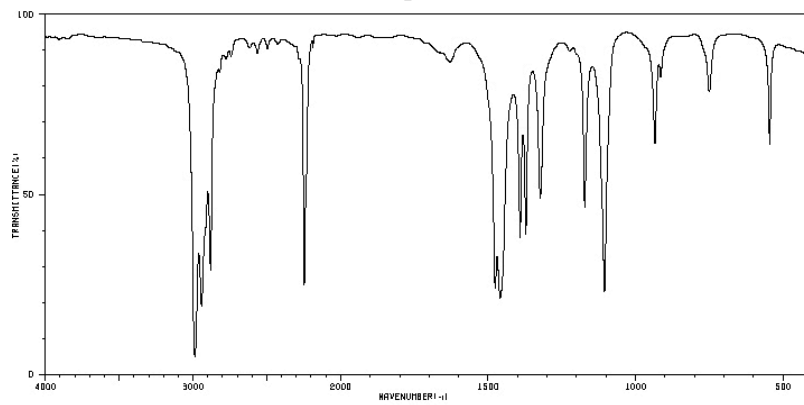
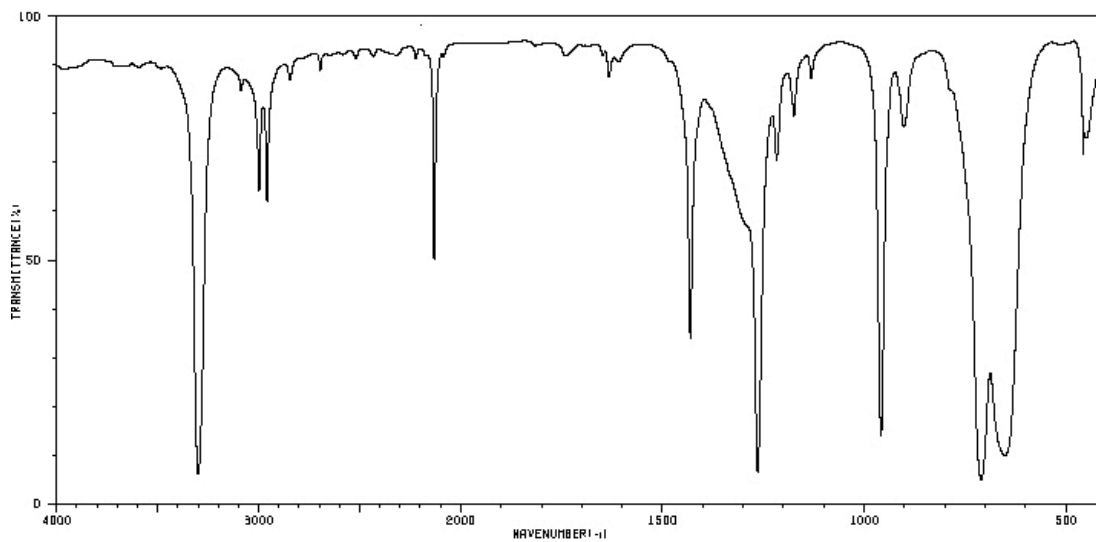

Cmpd **B**

Cmpd **C**

Cmpd **D**

Question 2. Some spectroscopic data for an unknown compound (**H**) are shown below. Use these data to answer the questions **on the following page**. (20 points)

Mass Spectrum

IR Spectrum

1H-NMR: δ = 2.24 (singlet, 1H), 3.94 (singlet, 2H) ppm

13C-NMR: δ = 30, 75, 79 ppm

3

(a) What is the molecular formula of compound **H**? (5 points)

(b) What is the structure of compound **H**? (10 points)

(c) What is the **precise** structure of the species that gives rise to the peak at $m/z = 74$? (1 points)

(d) What is the **precise** structure of the species that gives rise to the peak at $m/z = 75$? (1 point)

(e) What is the **precise** structure of the species that gives rise to the peak at $m/z = 76$? (1 point)

(f) What is the **precise** structure of the species that gives rise to the peak at $m/z = 77$? (1 point)

(g) What is the structure of the fragment that gives rise to the base peak at $m/z = 39$? (1 point)

Question 3. Some spectroscopic data for an unknown compound (**J**) are shown below. Use these data to answer the questions **on the following page**. (25 points)

Mass Spectrum
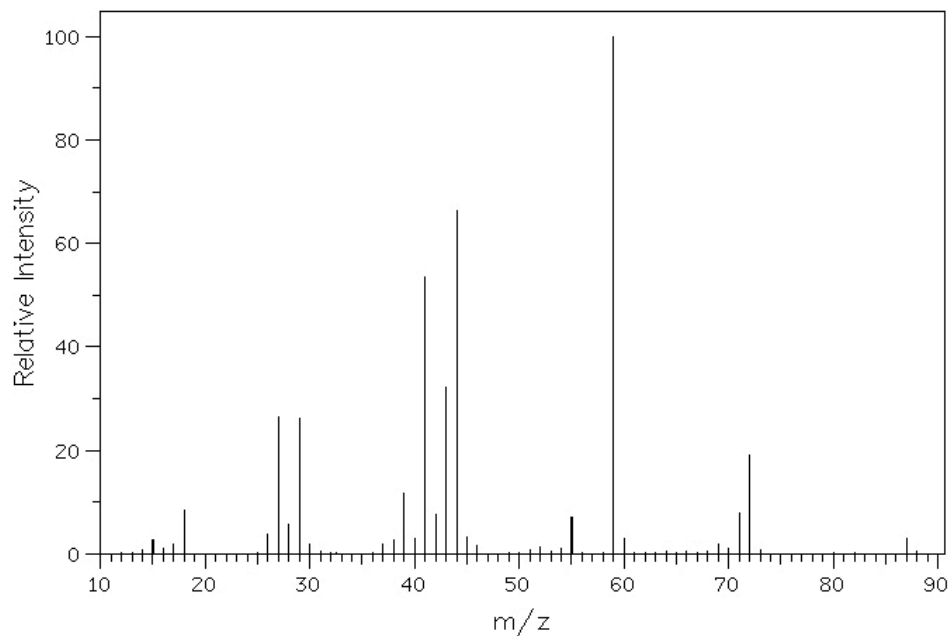
IR Spectrum
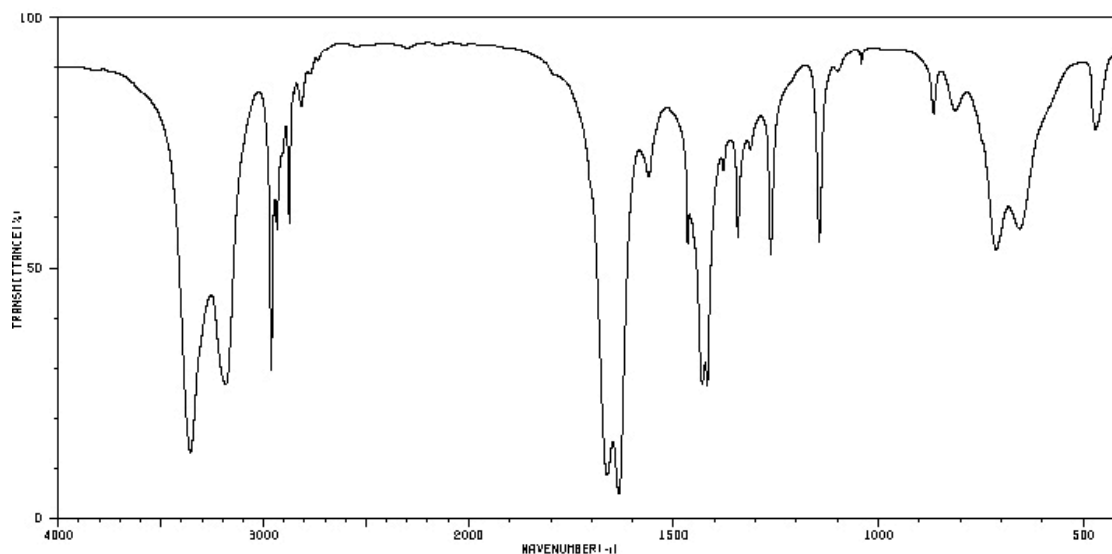
1H-NMR: δ = 0.86 (triplet, 3H), 1.50 (sextet, 2H), 2.02 (triplet, 2H), 6.96 (broad singlet, 2H) ppm

13C-NMR: δ = 14, 19, 38, 176 ppm

(a) What is the molecular formula of compound **J**? (5 points)

(b) What is the structure of compound **J**? (10 points)

(c) What is the structure of the fragment (**K**) that gives rise to the base peak at $m/z = 59$? (3 points)

(d) What is the name of the rearrangement that results in the formation of fragment **K**? (2 points)

(e) Draw the mechanism showing how **J** fragments to give **K**? (5 points)

Question 4.   The structure of methyl propionate is shown opposite.
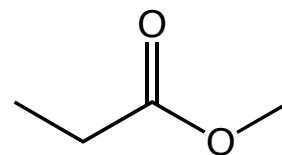
(a)   Draw the 1H-NMR spectrum of methyl propionate. (10 points)

```
10   9   8   7   6   5   4   3   2   1   0  ppm
```
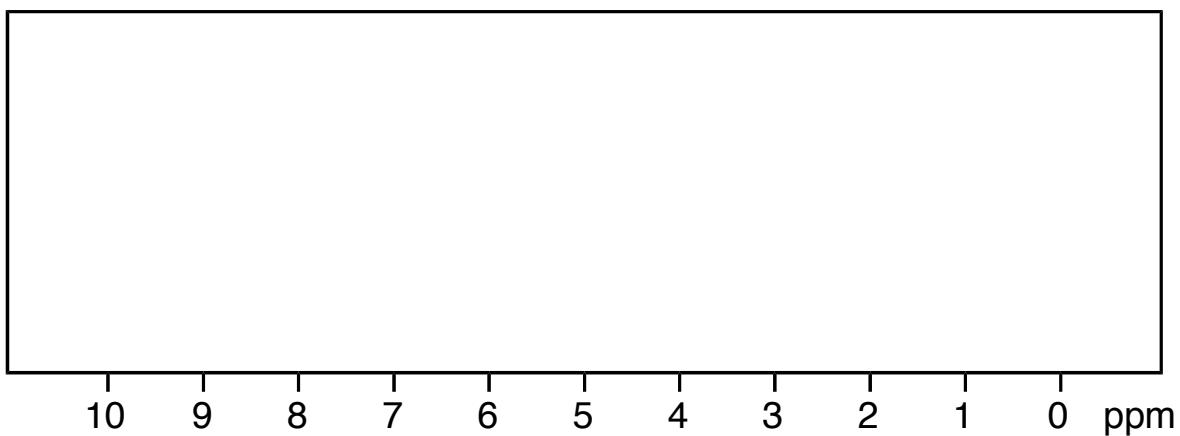
(b)   Draw the 1H-decoupled 13C-NMR spectrum of methyl propionate. (6 points)

```
200          150          100          50           0
```
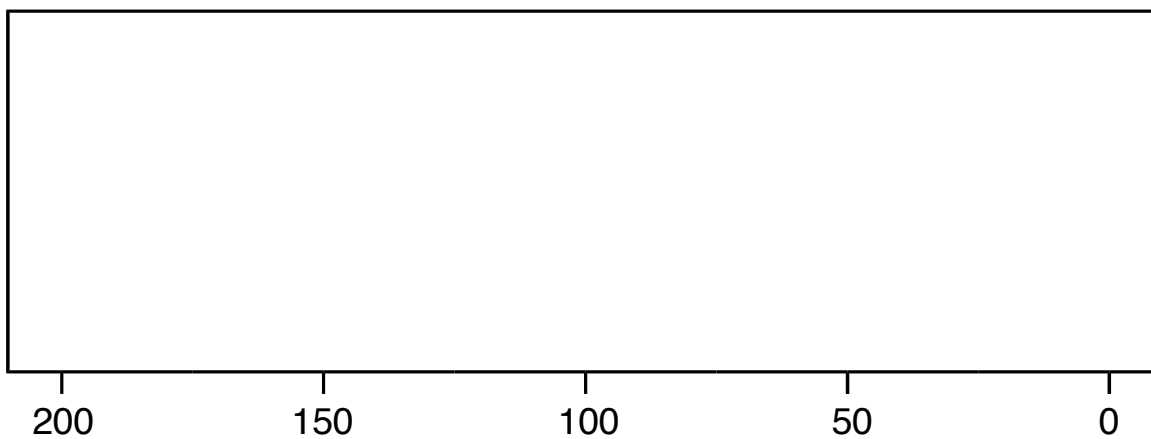
(c)   Draw the 13C-DEPT-NMR spectrum of methyl propionate. (4 points)

```
200          150          100          50           0
```
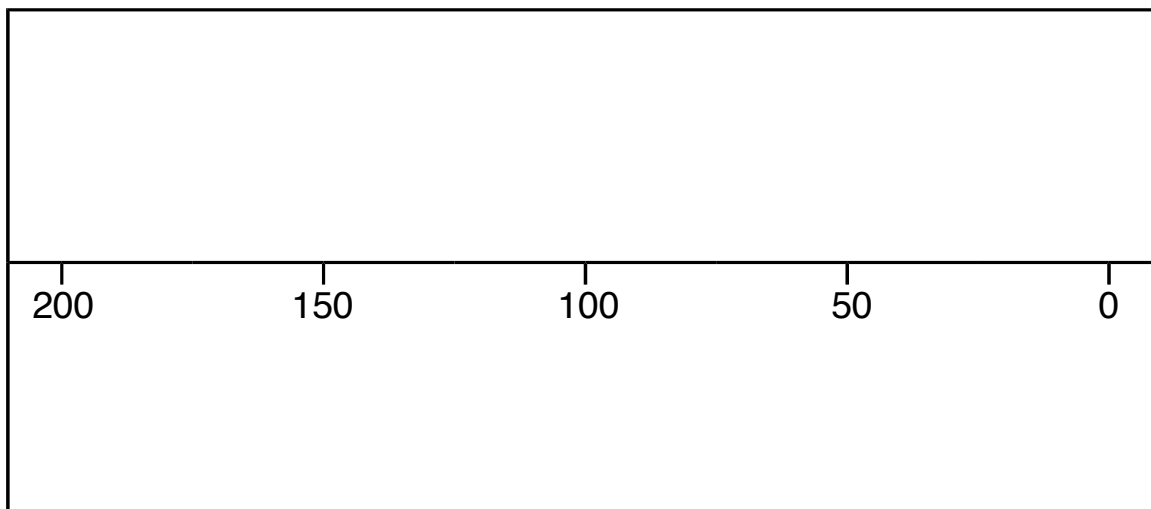
Question 5. The Wolff-Kishner reduction (shown below) converts a C=O group into a CH_2 group upon treatment with hydrazine (NH_2NH_2) and base (KOH) at elevated temperatures (>200 °C). What is the mechanism **for the second step in the reaction**, i.e., the decomposition of the hydrazone upon reaction with KOH? (14 points)
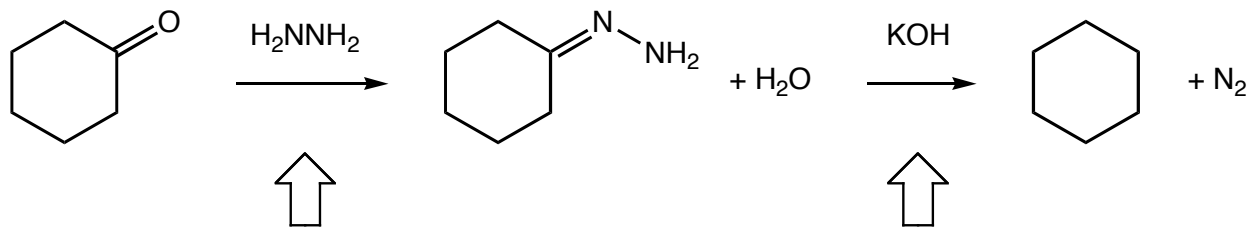
I DO NOT want you to write out the mechanism for this step

What's the mechanism for this step?

Question 6. Predict the number of signals you would expect to see in the 1H-decoupled 13C-NMR spectrum of each of the molecules shown below. (2 points each)

(a)
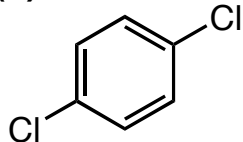
(b)
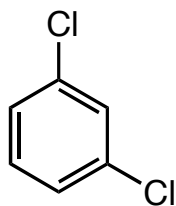
(c)
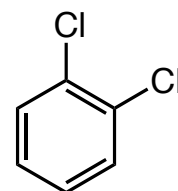
(d)
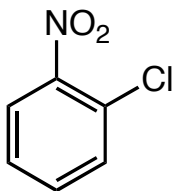
(e)
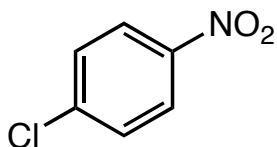
(f)
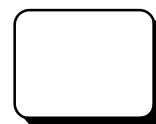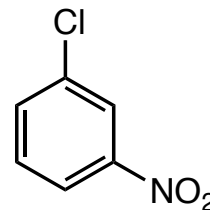
(f)
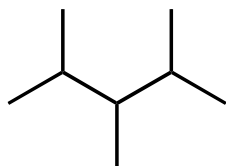
(g)
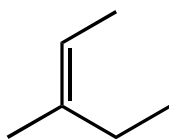
(h)
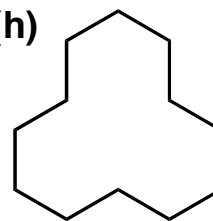
Question 7. Predict the MAJOR product for each of the reactions shown below? (2 points each)

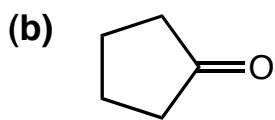**(a)** [cyclopentanone] $\xrightarrow[\text{H}_2\text{O}]{\text{Zn / HCl}}$ [   ]

(b) [cyclopentanone] $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) LiAlH}_4 \text{ / Et}_2\text{O}}$ [   ]

(c) [cyclopentanone] $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) NaBD}_4 \text{ / MeOH}}$ [   ]

(d) [cyclopentenone] $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) NaBH}_4 \text{ / MeOH}}$ [   ]

(e) [cyclopentenone] $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) LiAlH}_4 \text{ / Et}_2\text{O}}$ [   ]

(f) [cyclopentenone] $\xrightarrow[\text{(Ph}_3\text{P)}_3\text{RhCl}]{\text{H}_2}$ [   ]

(g) [cyclopentenone] $\xrightarrow{\text{H}_2 \text{ / Pt}}$ [   ]

(h) [cyclopentenone] $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) LiAlD}_4 \text{ / Et}_2\text{O}}$ [   ]

(i) [cyclopentenone] $\xrightarrow[\text{(ii) D}_3\text{O}^+]{\text{(i) NaBH}_4 \text{ / MeOH}}$ [   ]

10
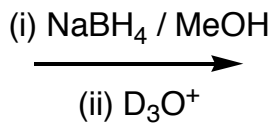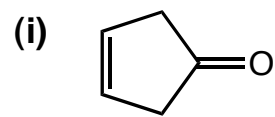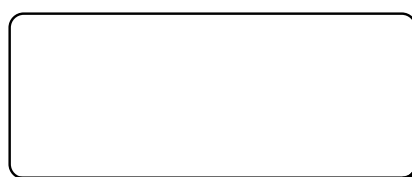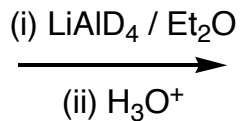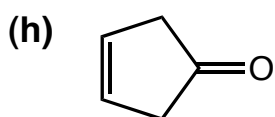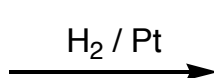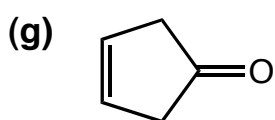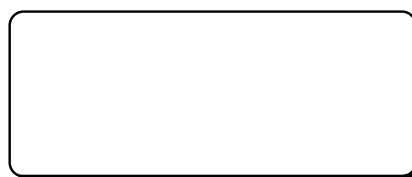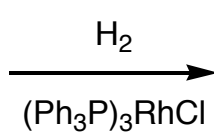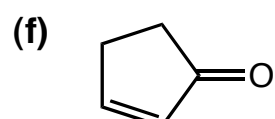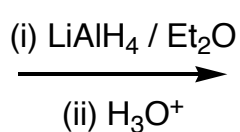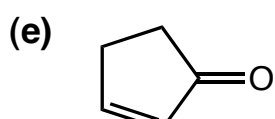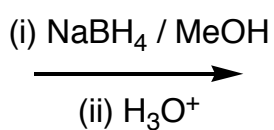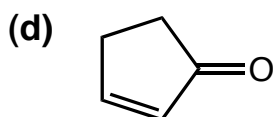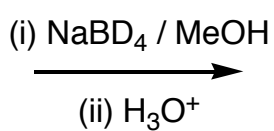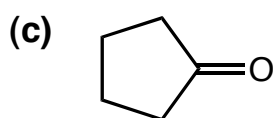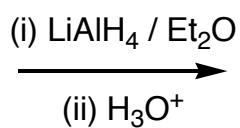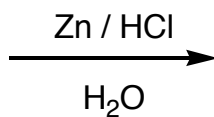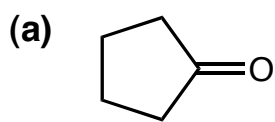
Question 8. For each of the three cyclobutane derivatives shown below, indicate the stereotopical relationships (HOMOTOPIC, ENANTIOTOPIC, DIASTEREOTOPIC) between the pairs of hydrogen atoms listed in each case? (1 point each)
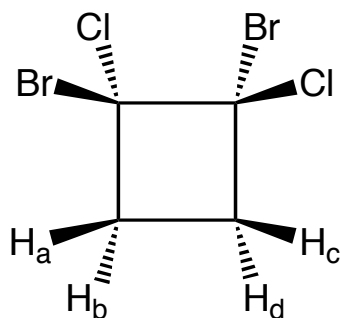
(a)

Br   Br
Cl   Cl

H$_a$ H$_c$
   H$_b$ H$_d$

H$_a$ and H$_b$ =

H$_a$ and H$_c$ =

H$_a$ and H$_d$ =

(b)

Cl   Br
Br   Cl

H$_a$ H$_c$
   H$_b$ H$_d$
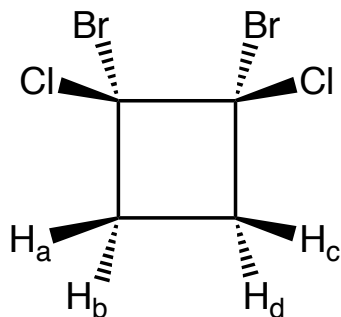
H$_a$ and H$_b$ =

H$_a$ and H$_c$ =

H$_a$ and H$_d$ =

(c)

Br   Cl
Br   Cl

H$_a$ H$_c$
   H$_b$ H$_d$
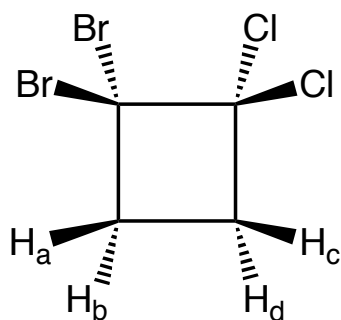
H$_a$ and H$_b$ =

H$_a$ and H$_c$ =

H$_a$ and H$_d$ =

Question 9. Propose a reasonable mechanism that accounts for the transformation shown in the box below. (10 points)

$$\text{H}_2\text{SO}_4$$
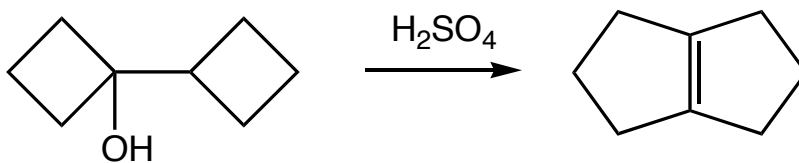
Question 10. Each of these reactions produces ONE MAJOR PRODUCT. In each case, draw this product (including appropriate stereochemistry where relevant) in the box provided. For multi-step reactions just give the FINAL product, i.e., no intermediates. (2 points each)

(a)

NH

H⁺ (cat)

(b)

Ph₂CuLi

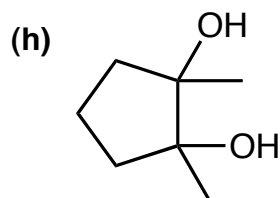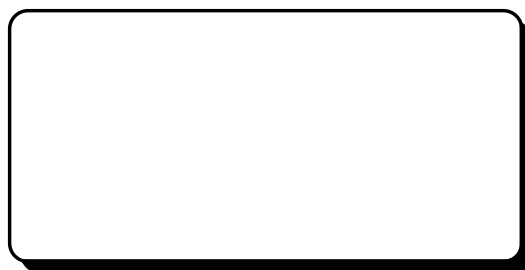THF (solvent)

(c)

HO

OH

OH

H₂CrO₄

(d)

HO   Cl

H₃C   D

D   CH₃

NaOH / H₂O

(e)

OH

O

H⁺ (cat)

(f)

O

O

(i) xs CH₃CH₂Li

(ii) H₃O⁺
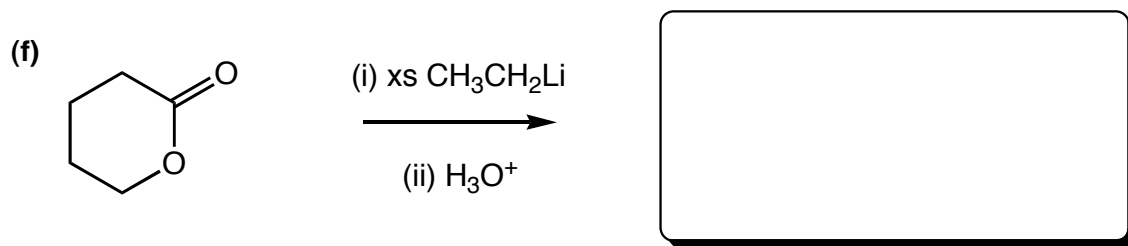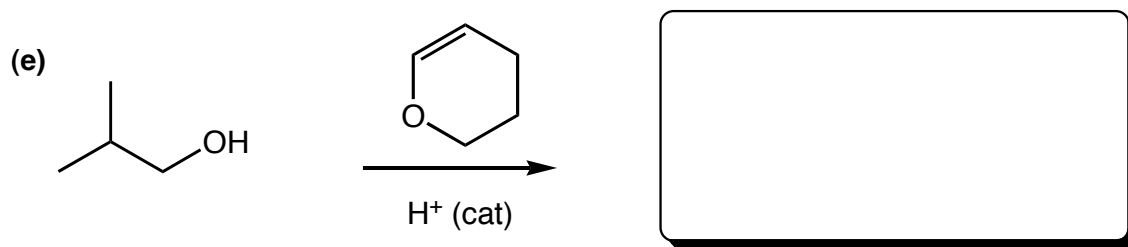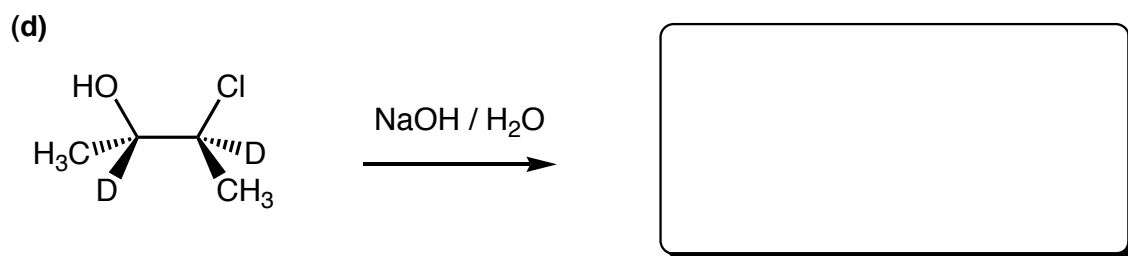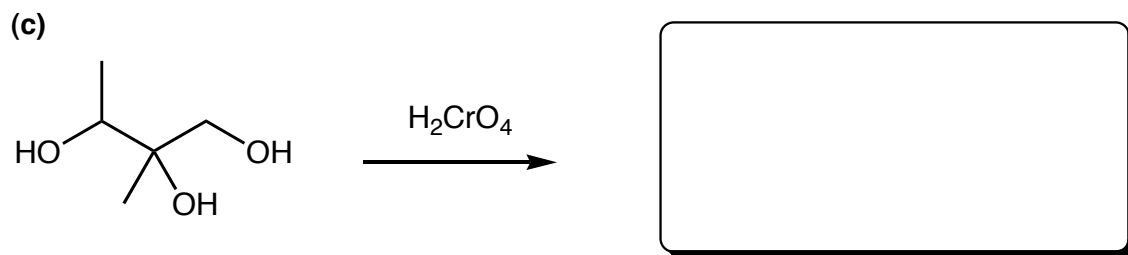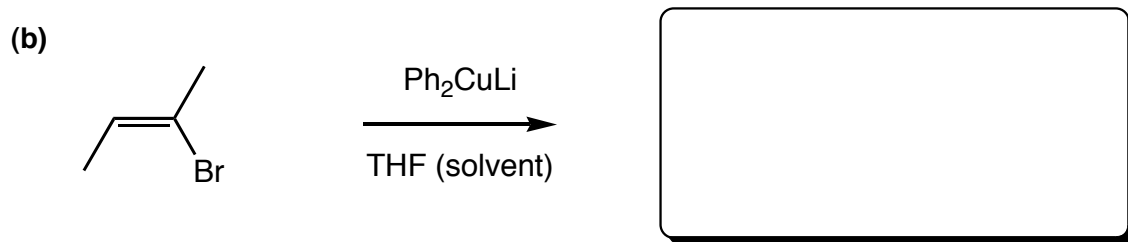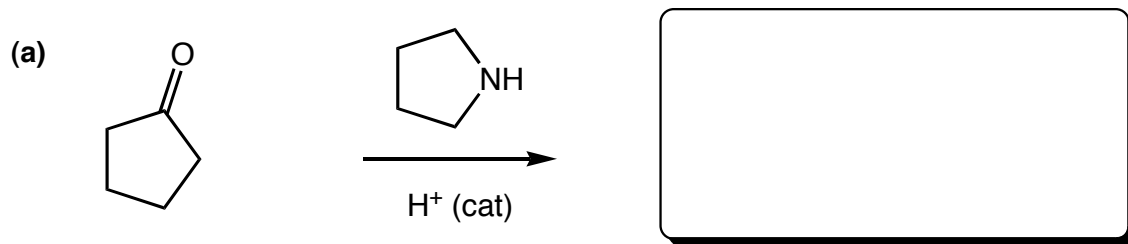
question 10 continues on the next page...

(g)

cyclobutylmethanol $\xrightarrow{H_3PO_4}$

(h)

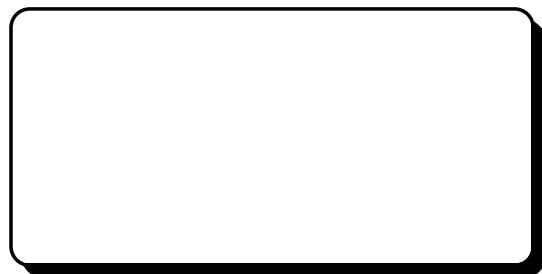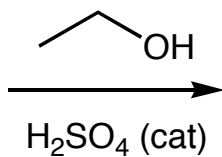1,2-dimethylcyclopentane-1,2-diol $\xrightarrow{H_2SO_4}$

(i)

cyclopentylmethanol $\xrightarrow[\text{(ii) } CH_3CH_2CH_2OMs]{\text{(i) NaH}}$

(j)

acetophenone $\xrightarrow{\text{mCPBA}}$

(k)

1-iodo-2-methylpropane $\xrightarrow[\text{(ii) NaOH / } H_2O]{\text{(i) thiourea}}$

(l)

methylenecyclopentane $\xrightarrow[\text{Cu/Zn}]{CH_2I_2}$

(m)

H_2SO_4 (cat)

CH₃CH₂OH drawn as ⌃⌄OH

(n)

⊕
—PPh₃

NaH

(o)

(i) NaOEt

(ii) H_2O

(p)

MeOH / H⁺

(q)

HBr

(r)

OMe

Cy₃P
Cl
Ru
Cl
PCy₃   Ph

CH_2Cl_2
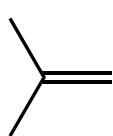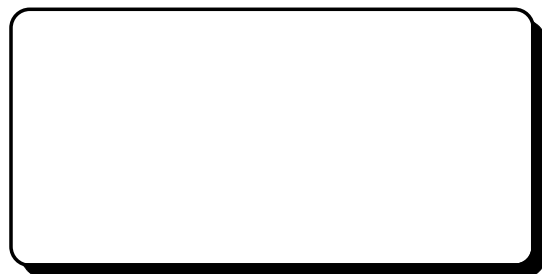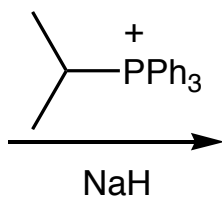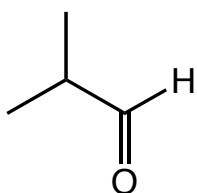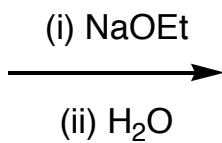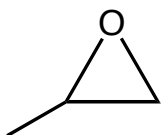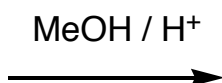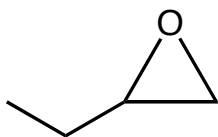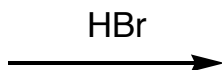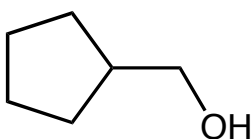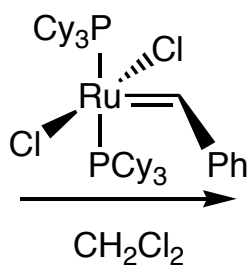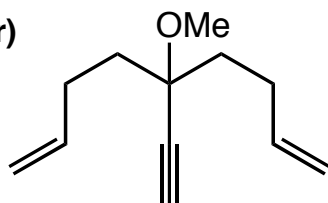
Question 11. (BONUS) Propose a synthesis of 2-butanone using acetaldehyde as your only source of carbon atoms (i.e., all of the C atoms in your product muct originate from acetaldehyde). You may use any other reagents of your choosing, however, if the reagents contain carbon and form part of your product you must make these reagents from acetaldehyde!). Show all intermediates and reagents for each transformation. DO NOT SHOW MECHANISMS! (14 points)

acetaldehyde   many steps   2-butanone
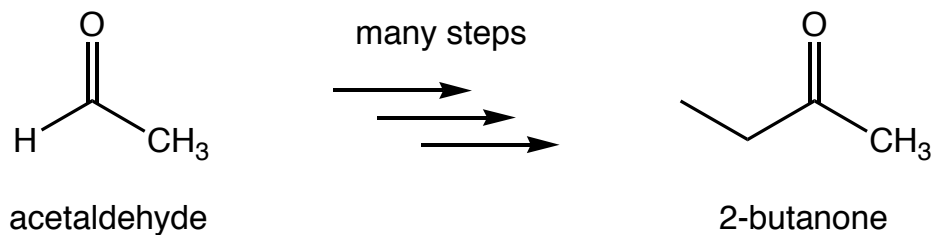
Question 12. (BONUS) When D-Threitol reacts with formaldehyde, three isomeric products are formed, **A**, **B**, and **C**. Each of these products has the formula $C_6H_{10}O_4$, and contains two rings. Propose structures for **A**, **B**, and **C**. (3 points each)

OH

HO$\diagdown\diagup\diagdown\diagup\diagdown$OH + (formaldehyde structure) $\xrightarrow{\text{H}^+\text{ (cat)}}$ **Three Products (A, B, C)**

OH

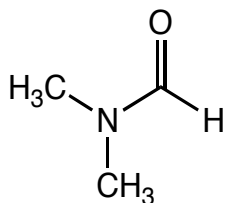H$\diagup^{\text{O}}\diagdown$H

D-Threitol   Formaldehyde

A

B

C
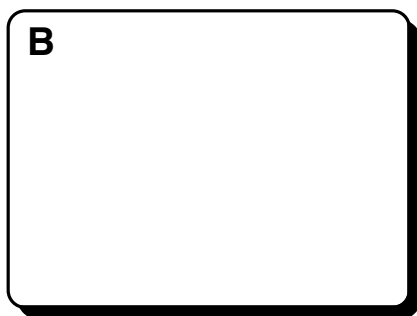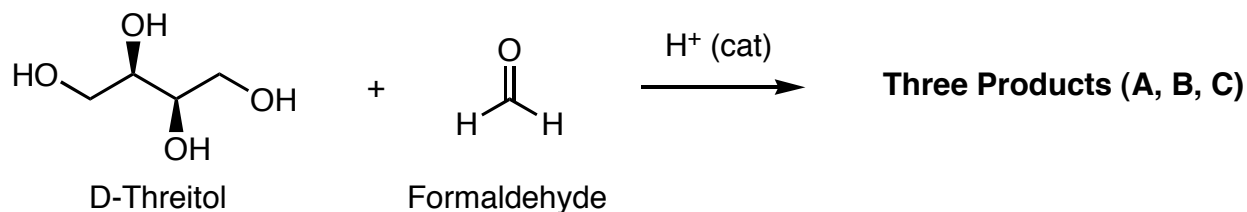
If the mixture of products **A**, **B**, and **C** above, are heated in the presence of an acid catalyst for an extended amount of time the system converges to one single product (i.e., two of the products are converted into the third). In this case, what is the structure of this exclusive product and explain why it is the sole product under these conditions? (3 points)

Question 13. (BONUS) Explain why the 1H-NMR spectrum of dimethylformamide contains two methyl singlets at room temperature, but only one at elevated temperatures? (4 points)

H$_3$C$\diagdown$N$\diagup^{\text{O}}\diagdown$H

CH$_3$

Dimethylformamide