

Name: _____

CHEM 322. Midterm 2
Spring 2014
Watson, Hietbrink

Please write your answers clearly in the boxes provided. If your answer is illegible or outside the box, it will not be graded. You may use the back of test pages for scratch work.

You may use molecular models.

Use of calculators, cell phones, headphones, or any other electronic device during this exam is prohibited.

No notes or books may be used during this exam. Tables of spectral data and a periodic table are provided at the end of this exam.

You may raise your hand to ask a question if you are not sure what is being asked of you.

There are -- pages in this exam. Please check that your test has -- pages before you begin. The last 2 pages are blank and may be used as scratch paper.

Please circle your lecture:

Hietbrink 8:00 AM class

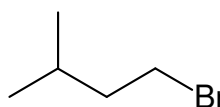
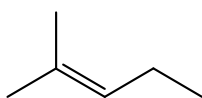
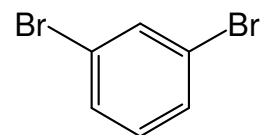
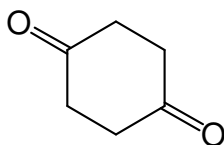
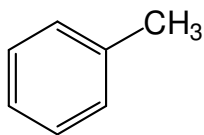
Hietbrink 11:15 AM class

Watson class

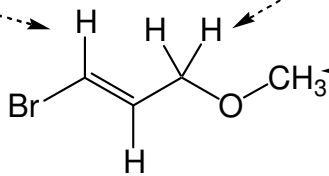
| Question | Points |
|-----------------|---------------|
| 1 | ____ /25 |
| 2 | ____ /20 |
| 3 | ____ /20 |
| 4 | ____ /10 |
| 5 | ____ /40 |
| 6 | ____ /30 |
| 7 | ____ /15 |
| 8 | ____ /50 |
| 9 | ____ /40 |
| Total | ____ /250 |

Name: _____

1. (25 points) Predict how many signals you would see in the ^{13}C spectrum of each of these molecules. Put your answer in the box below the molecule.



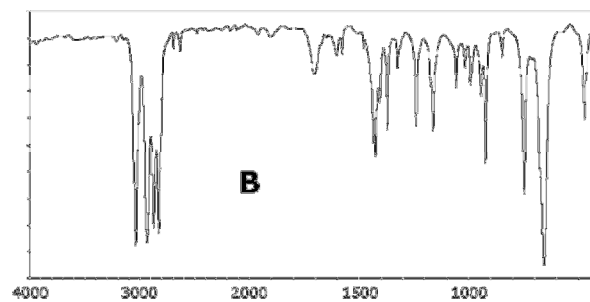
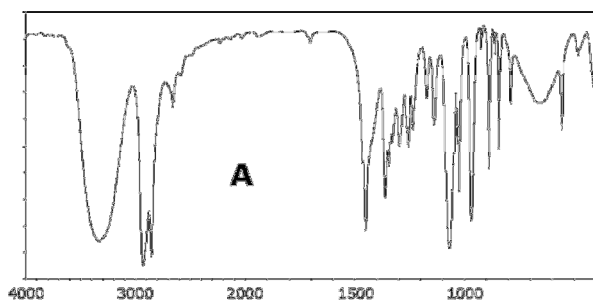
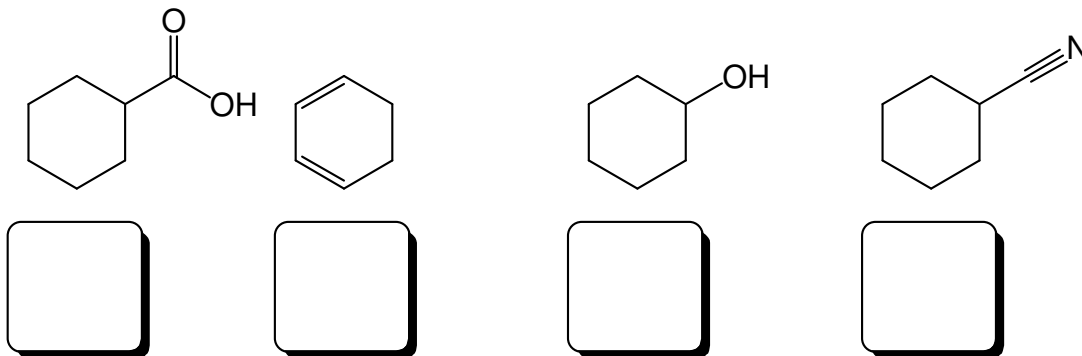
2. (20 points) The ^1H NMR of this compound should have four signals. Predict the splitting pattern (singlet, doublet, doublet of doublets, etc) you would see for each signal.



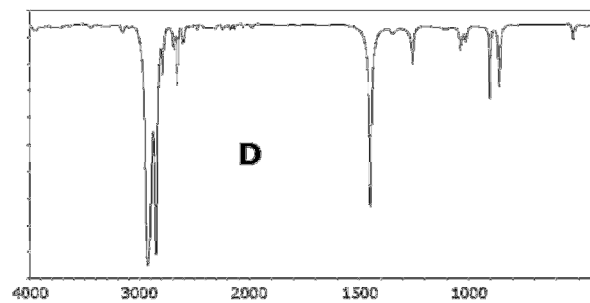
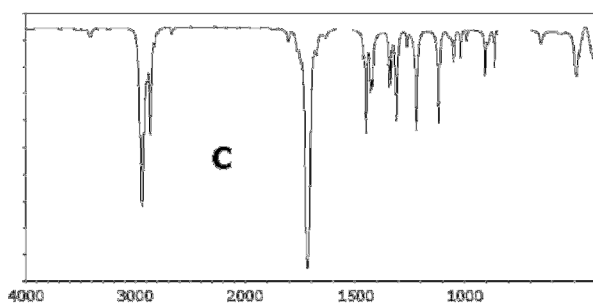
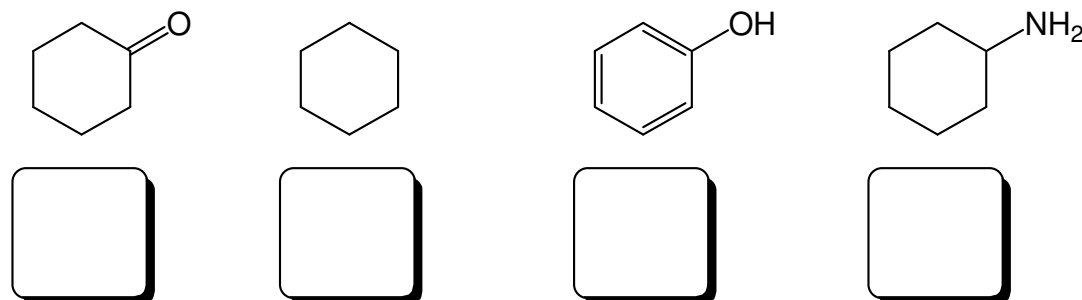
Name: _____

3. (20 points) Below are the IR spectra for four of these eight compounds. Put the letter of the spectrum in the box below the appropriate compound.

a) Spectra A and B refer to two of these four compounds.

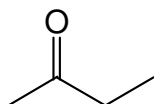


b) Spectra A and B refer to two of these four compounds.



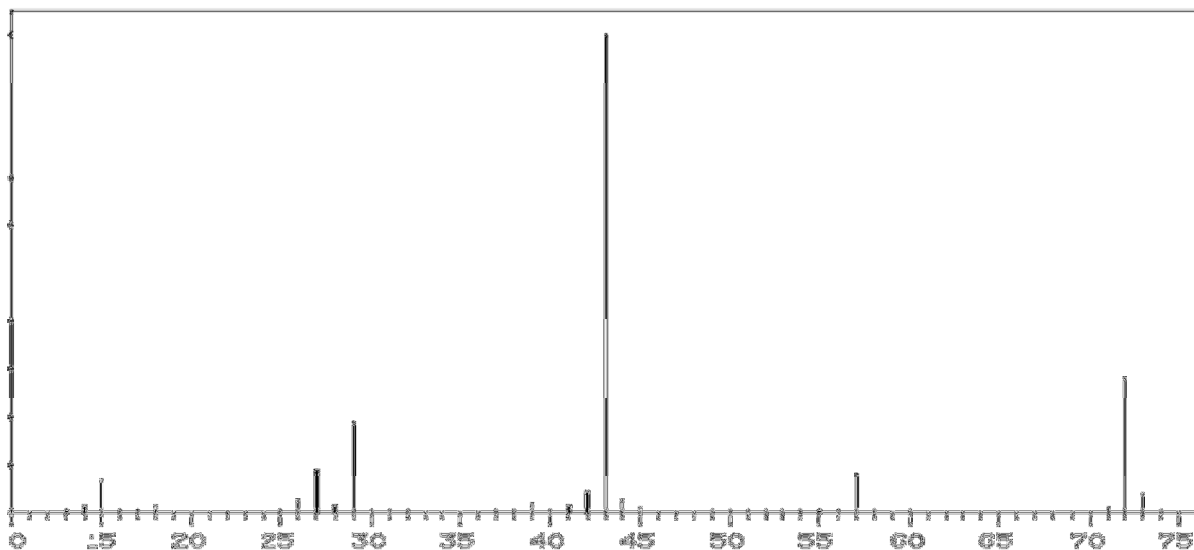
Name: _____

4. (10 points) Below is the mass spectrum of 2-butanone. In the boxes, explain the large peak at 43 and the small peak at 73.



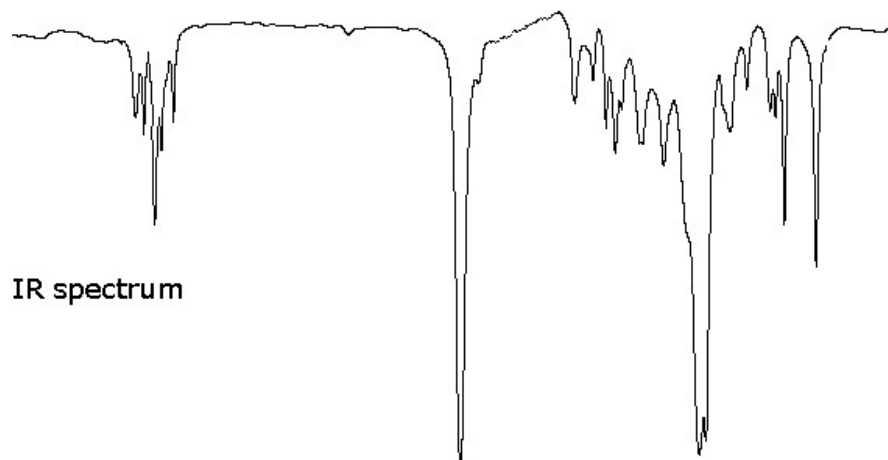
43

73



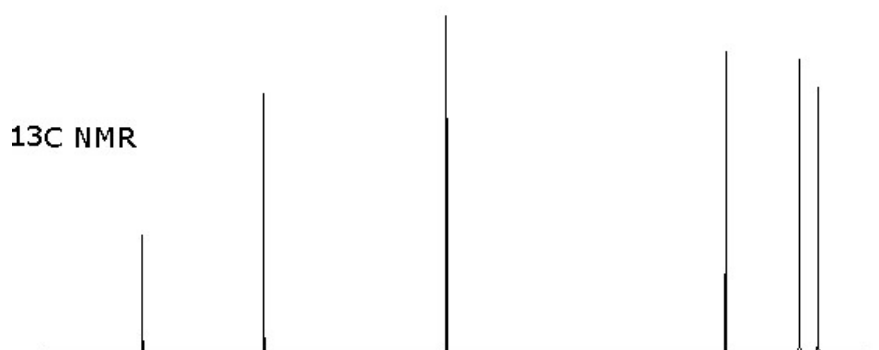
Name: _____

5. (40 points) Here are the IR, ^{13}C NMR, and ^1H NMR spectra for an unknown with the formula $\text{C}_6\text{H}_{10}\text{O}_2$. Answer questions on the next page.



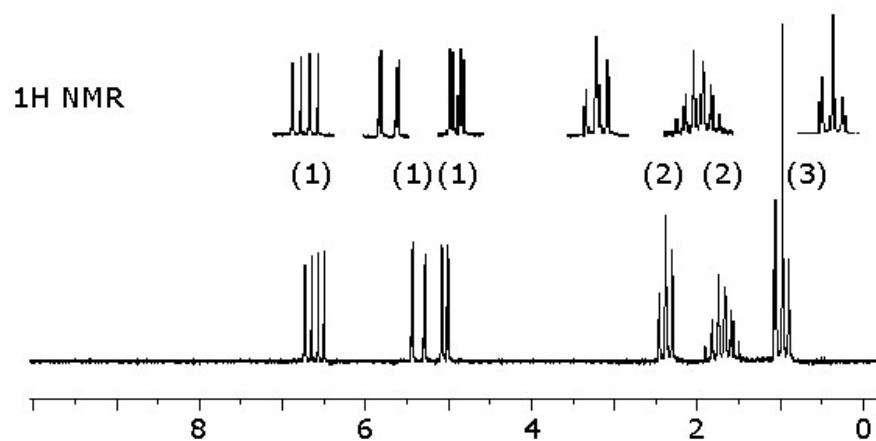
IR spectrum

3500 3000 2000 1500 1000



^{13}C NMR

200 150 100 50 0



^1H NMR

(1) (1) (1) (2) (2) (3)

C

Name: _____

5 continued. (40 points) These questions all refer to the spectra on the previous page.

a) How many degrees of unsaturation are in this compound?

b) Is there symmetry in this compound?

c) In the IR, what does the signal at about 1740 suggest?

d) In the ^{13}C NMR, what does the chemical shift of the signal at about 105 suggest?

e) In the ^1H NMR, what does the chemical shift of the signal at about 5.2 suggest?

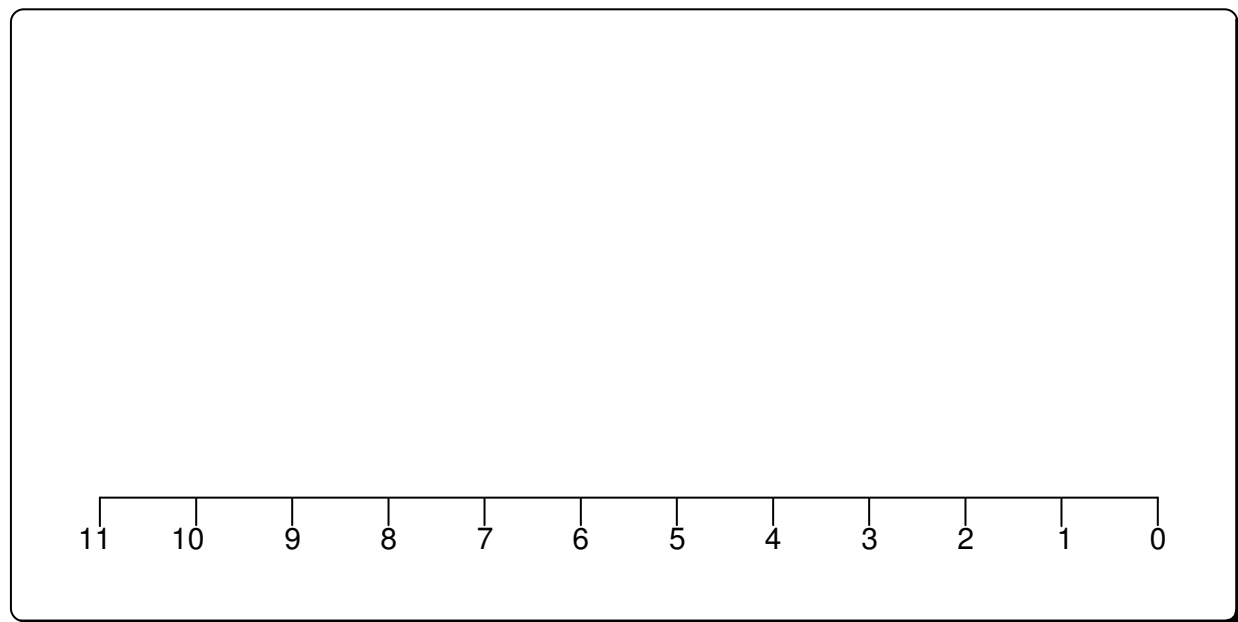
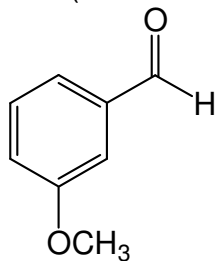
f) In the ^1H NMR, what does the integration of the signal at about 2.3 suggest?

g) In the ^1H NMR, what does the splitting pattern of the signal at about 1.0 suggest?

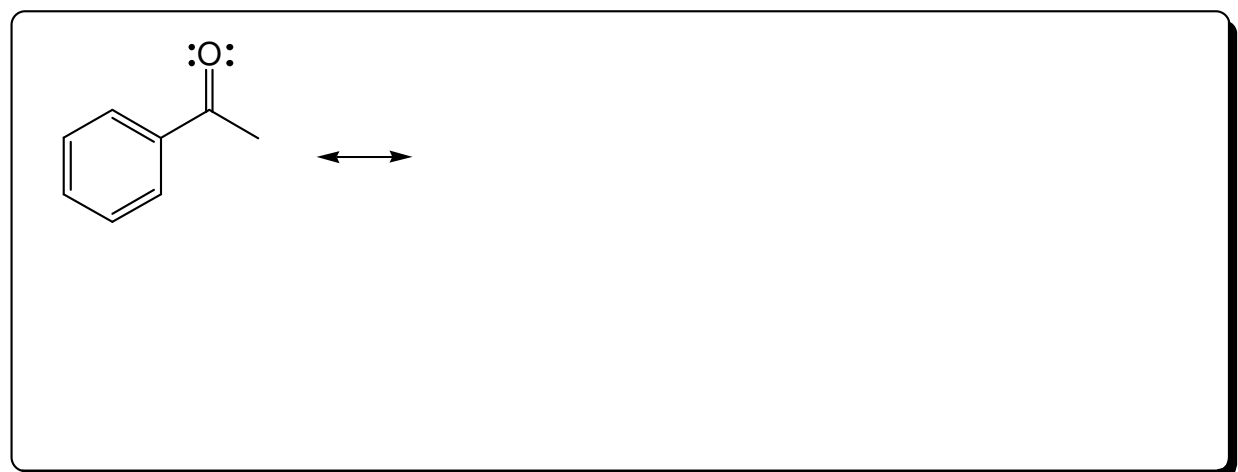
h) What is the structure of this unknown?

Name: _____

6. (30 points) Draw what you would expect to see in the ^1H NMR of this compound. Your drawing should clearly show the number of signals, their approximate chemical shift (within 1 PPM) and the expected splitting pattern.

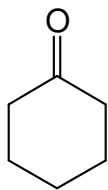


7. (15 points) Draw the important resonance structures for this compound.

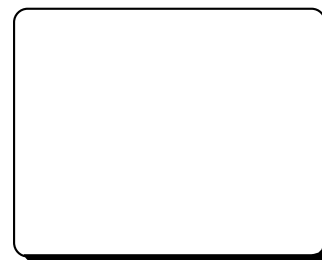
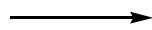
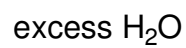
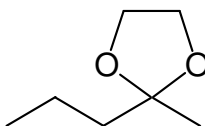
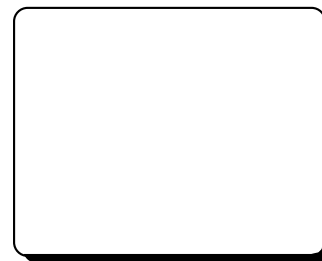
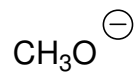
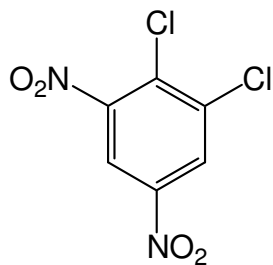
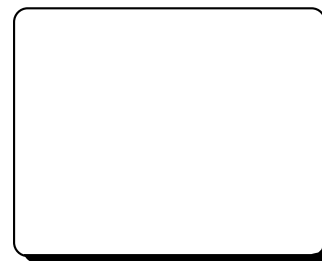
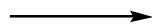
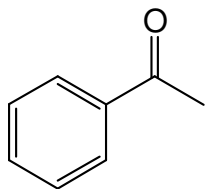
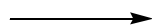
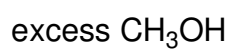
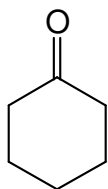
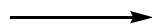


Name: _____

8. (50 points) Predict the major organic product or products for the following reactions.

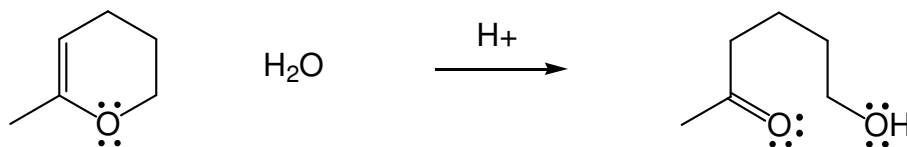


heat



Name: _____

9. (40 points) Please draw a reasonable arrow-pushing mechanism for the following reaction.



Blank area for drawing the arrow-pushing mechanism.

Name: _____

Approximate IR Absorption Frequencies


| Bond | Frequency (cm ⁻¹) | Intensity |
|-----------------------|-------------------------------|--------------------|
| O-H (alcohol) | 3650–3200 | Strong, broad |
| O-H (carboxylic acid) | 3300–2500 | Strong, very broad |
| N-H | 3500–3300 | Medium, broad |
| C-H | 3300–2700 | Medium |
| C≡N | 2260–2220 | Medium |
| C≡C | 2260–2100 | Medium to weak |
| C=O | 1780–1650 | Strong |
| C-O | 1250–1050 | Strong |

Approximate ¹H NMR Chemical Shifts

| Hydrogen | δ (ppm) |
|----------------------------------|----------|
| CH ₃ | 0.8–1.0 |
| CH ₂ | 1.2–1.5 |
| CH | 1.4–1.7 |
| C=C-CH _x | 1.7–2.3 |
| O=C-CH _x | 2.0–2.7 |
| Ph-CH _x | 2.3–3.0 |
| ≡C-H | 2.5 |
| R ₂ N-CH _x | 2.0–2.7 |
| I-CH _x | 3.2 |
| Br-CH _x | 3.4 |
| Cl-CH _x | 3.5 |
| F-CH _x | 4.4 |
| O-CH _x | 3.2–3.8 |
| C=CH | 4.5–7.5 |
| Ar-H | 6.8–8.5 |
| O=CH | 9.0–10.0 |
| ROH | 1.0–5.5 |
| ArOH | 4.0–12.0 |
| RNH _x | 0.5–5.0 |
| CONH _x | 5.0–10.0 |
| RCOOH | 10–13 |

Approximate ¹³C NMR Chemical Shifts

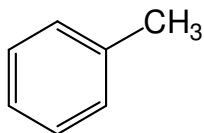
| Carbon | δ (ppm) |
|-------------------------|---------|
| <i>Alkanes</i> | |
| Methyl | 0–30 |
| Methylene | 15–55 |
| Methine | 25–55 |
| Quaternary | 30–40 |
| <i>Alkenes</i> | |
| C=C | 80–145 |
| <i>Alkynes</i> | |
| C≡C | 70–90 |
| <i>Aromatics</i> | |
| Benzene | 128.7 |
| <i>Alcohols, Ethers</i> | |
| C-O | 50–90 |
| <i>Amines</i> | |
| C-N | 40–60 |
| <i>Halogens</i> | |
| C-F | 70–80 |
| C-Cl | 25–50 |
| C-Br | 10–40 |
| C-I | -20–10 |
| <i>Carbonyls, C=O</i> | |
| R ₂ C=O | 190–220 |
| RXC=O (X = O or N) | 150–180 |



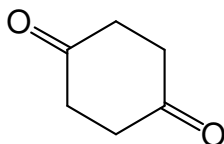
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|-----|-----|----|--------|-----|----|--------|-----|-------|---------|-------|--------|---------|
| 1 | 1 | H | 1.008 | 2 | | 13 | B | 10.81 | 14 | C | 12.011 | |
| 2 | 3 | Li | 6.941 | 4 | Be | 9.012 | 5 | | 6 | | | |
| 3 | 7 | Na | 22.989 | 8 | Mg | 24.305 | 9 | | 10 | Al | 26.982 | |
| 4 | 11 | K | 39.098 | 12 | Ca | 40.08 | 13 | Sc | 44.96 | 14 | Ti | 47.88 |
| 5 | 15 | Rb | 85.468 | 16 | Sr | 87.62 | 17 | Y | 88.906 | 18 | Zr | 91.224 |
| 6 | 19 | Cs | 132.9 | 20 | Ba | 137.3 | 21 | La | 138.9 | 22 | Hf | 178.49 |
| 7 | 23 | Fr | (223) | 24 | Ra | (226) | 25 | Ac | (227) | 26 | Rf | (261) |
| 8 | 27 | | | 28 | | | 29 | Pr | (140.9) | 30 | Nd | (144.2) |
| 9 | 31 | | | 32 | | | 33 | Pm | (145) | 34 | Sm | (150.4) |
| 10 | 35 | | | 36 | | | 37 | Eu | (152) | 38 | Gd | (157.3) |
| 11 | 39 | | | 40 | | | 41 | Tb | (158.9) | 42 | Dy | (162.5) |
| 12 | 43 | | | 44 | | | 45 | Ho | (164.9) | 46 | Er | (167.3) |
| 13 | 47 | | | 48 | | | 49 | | | 50 | | |
| 14 | 51 | | | 52 | | | 53 | | | 54 | | |
| 15 | 55 | | | 56 | | | 57 | | | 58 | | |
| 16 | 59 | | | 60 | | | 61 | | | 62 | | |
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| 19 | 71 | | | 72 | | | 73 | | | 74 | | |
| 20 | 75 | | | 76 | | | 77 | | | 78 | | |
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| 22 | 83 | | | 84 | | | 85 | | | 86 | | |
| 23 | 87 | | | 88 | | | 89 | | | 90 | | |
| 24 | 91 | | | 92 | | | 93 | | | 94 | | |
| 25 | 95 | | | 96 | | | 97 | | | 98 | | |
| 26 | 99 | | | 100 | | | 101 | | | 102 | | |
| 27 | 103 | | | 104 | | | 105 | | | 106 | | |
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| 30 | 115 | | | 116 | | | 117 | | | 118 | | |
| 31 | 119 | | | 120 | | | 121 | | | 122 | | |
| 32 | 123 | | | 124 | | | 125 | | | 126 | | |
| 33 | 127 | | | 128 | | | 129 | | | 130 | | |
| 34 | 131 | | | 132 | | | 133 | | | 134 | | |
| 35 | 135 | | | 136 | | | 137 | | | 138 | | |
| 36 | 139 | | | 140 | | | 141 | | | 142 | | |
| 37 | 143 | | | 144 | | | 145 | | | 146 | | |
| 38 | 147 | | | 148 | | | 149 | | | 150 | | |
| 39 | 151 | | | 152 | | | 153 | | | 154 | | |
| 40 | 155 | | | 156 | | | 157 | | | 158 | | |
| 41 | 159 | | | 160 | | | 161 | | | 162 | | |
| 42 | 163 | | | 164 | | | 165 | | | 166 | | |
| 43 | 167 | | | 168 | | | 169 | | | 170 | | |
| 44 | 171 | | | 172 | | | 173 | | | 174 | | |
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| 56 | 219 | | | 220 | | | 221 | | | 222 | | |
| 57 | 223 | | | 224 | | | 225 | | | 226 | | |
| 58 | 227 | | | 228 | | | 229 | | | 230 | | |
| 59 | 231 | | | 232 | | | 233 | | | 234 | | |
| 60 | 235 | | | 236 | | | 237 | | | 238 | | |
| 61 | 239 | | | 240 | | | 241 | | | 242 | | |
| 62 | 243 | | | 244 | | | 245 | | | 246 | | |
| 63 | 247 | | | 248 | | | 249 | | | 250 | | |
| 64 | 251 | | | 252 | | | 253 | | | 254 | | |
| 65 | 255 | | | 256 | | | 257 | | | 258 | | |
| 66 | 259 | | | 260 | | | 261 | | | 262 | | |
| 67 | 263 | | | 264 | | | 265 | | | 266 | | |
| 68 | 267 | | | 268 | | | 269 | | | 270 | | |
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| 70 | 275 | | | 276 | | | 277 | | | 278 | | |
| 71 | 279 | | | 280 | | | 281 | | | 282 | | |
| 72 | 283 | | | 284 | | | 285 | | | 286 | | |
| 73 | 287 | | | 288 | | | 289 | | | 290 | | |
| 74 | 291 | | | 292 | | | 293 | | | 294 | | |
| 75 | 295 | | | 296 | | | 297 | | | 298 | | |
| 76 | 299 | | | 300 | | | 301 | | | 302 | | |
| 77 | 303 | | | 304 | | | 305 | | | 306 | | |
| 78 | 307 | | | 308 | | | 309 | | | 310 | | |
| 79 | 311 | | | 312 | | | 313 | | | 314 | | |
| 80 | 315 | | | 316 | | | 317 | | | 318 | | |
| 81 | 319 | | | 320 | | | 321 | | | 322 | | |
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| 83 | 327 | | | 328 | | | 329 | | | 330 | | |
| 84 | 331 | | | 332 | | | 333 | | | 334 | | |
| 85 | 335 | | | 336 | | | 337 | | | 338 | | |
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| 88 | 347 | | | 348 | | | 349 | | | 350 | | |
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| 90 | 355 | | | 356 | | | 357 | | | 358 | | |
| 91 | 359 | | | 360 | | | 361 | | | 362 | | |
| 92 | 363 | | | 364 | | | 365 | | | 366 | | |
| 93 | 367 | | | 368 | | | 369 | | | 370 | | |
| 94 | 371 | | | 372 | | | 373 | | | 374 | | |
| 95 | 375 | | | 376 | | | 377 | | | 378 | | |
| 96 | 379 | | | 380 | | | 381 | | | 382 | | |
| 97 | 383 | | | 384 | | | 385 | | | 386 | | |
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| 100 | 395 | | | 396 | | | 397 | | | 398 | | |
| 101 | 399 | | | 400 | | | 401 | | | 402 | | |
| 102 | 403 | | | 404 | | | 405 | | | 406 | | |
| 103 | 407 | | | 408 | | | 409 | | | 410 | | |
| 104 | 411 | | | 412 | | | 413 | | | 414 | | |
| 105 | 415 | | | 416 | | | 417 | | | 418 | | |
| 106 | 419 | | | 420 | | | 421 | | | 422 | | |
| 107 | 423 | | | 424 | | | 425 | | | 426 | | |
| 108 | 427 | | | 428 | | | 429 | | | 430 | | |
| 109 | 431 | | | 432 | | | 433 | | | 434 | | |
| 110 | 435 | | | 436 | | | 437 | | | 438 | | |
| 111 | 439 | | | 440 | | | 441 | | | 442 | | |
| 112 | 443 | | | 444 | | | 445 | | | 446</ | | |

Name: _____

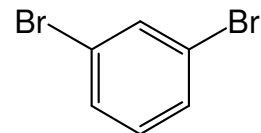
1. (25 points) Predict how many signals you would see in the ^{13}C spectrum of each of these molecules. Put your answer in the box below the molecule.



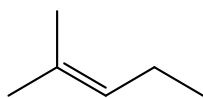
5



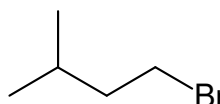
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4



6

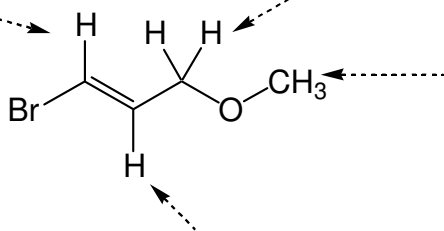


4

2. (20 points) The ^1H NMR of this compound should have four signals. Predict the splitting pattern (singlet, doublet, doublet of doublets, etc) you would see for each signal.

doublet

doublet



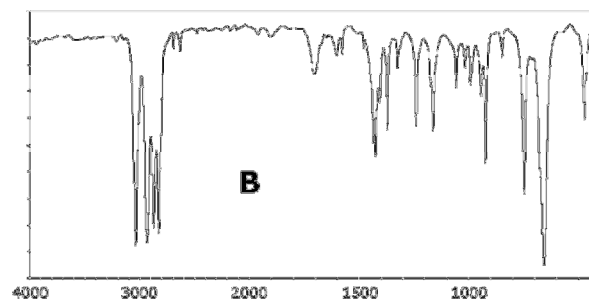
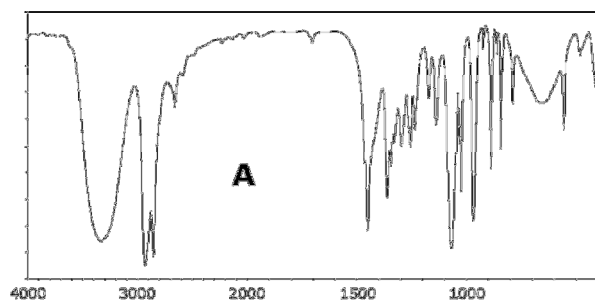
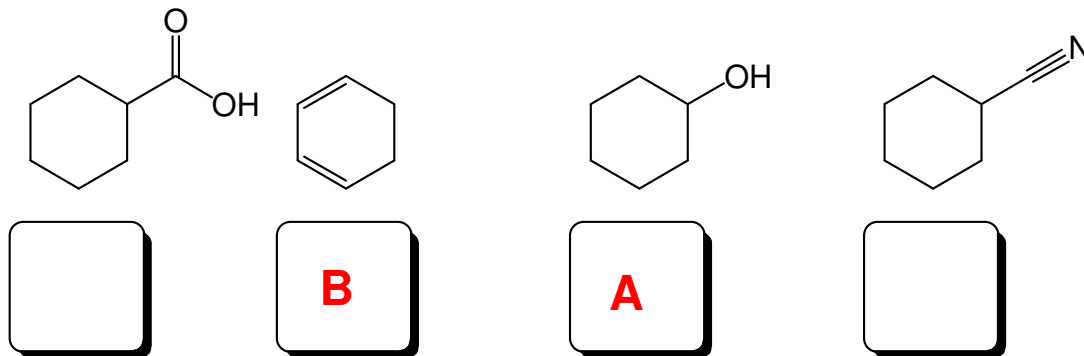
singlet

doublet of triplets or triplet of doublets

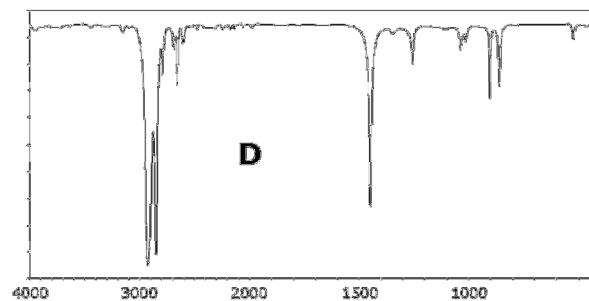
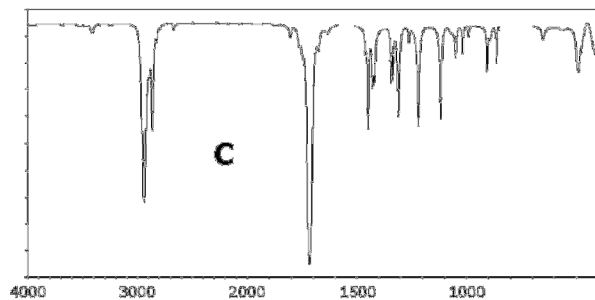
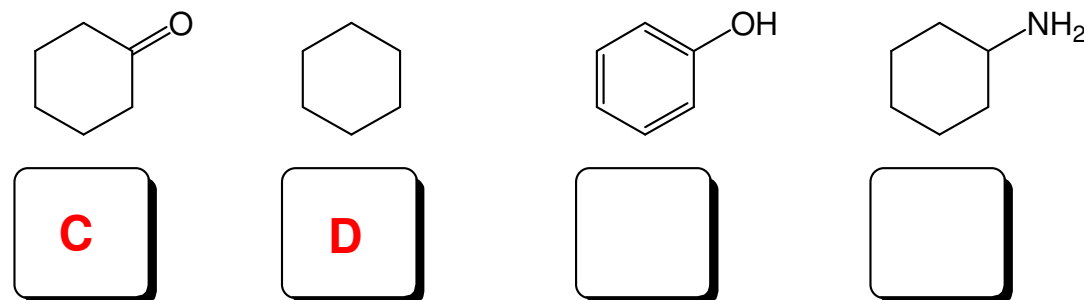
Name: _____

3. (20 points) Below are the IR spectra for four of these eight compounds. Put the letter of the spectrum in the box below the appropriate compound.

c) Spectra A and B refer to two of these four compounds.

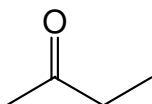


d) Spectra A and B refer to two of these four compounds.



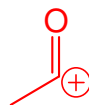
Name: _____

4. (10 points) Below is the mass spectrum of 2-butanone. In the boxes, explain the large peak at 43 and the small peak at 73.



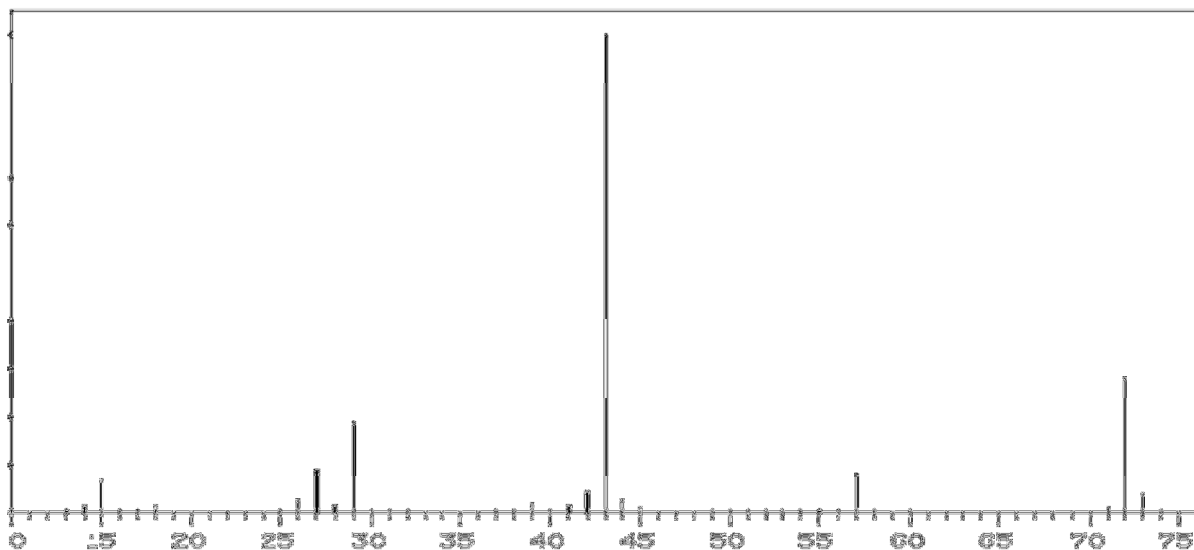
43

This is the base peak, the most common fragment. This comes from cleaving one of the bonds next to the carbonyl to give this:



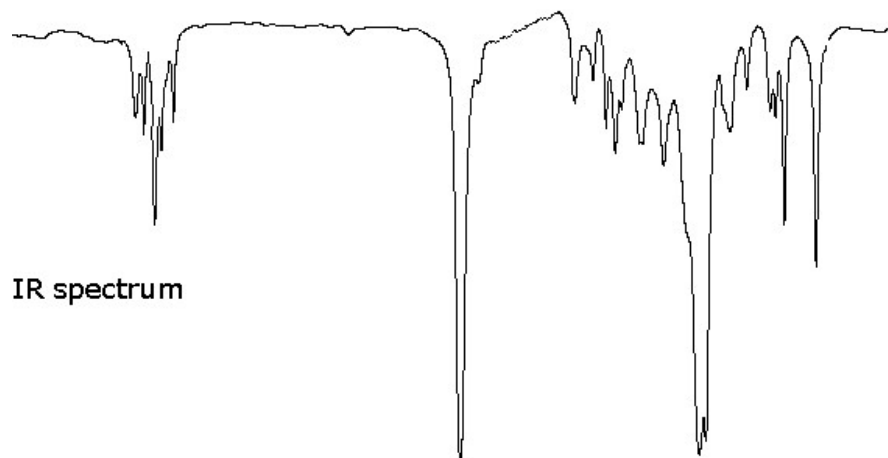
73

This is the M+1 peak. It is just the molecule (minus one electron), where one of the carbons is ¹³C.



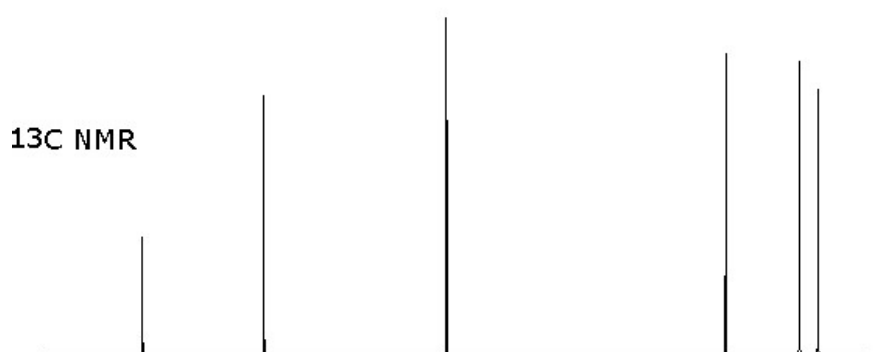
Name: _____

5. (40 points) Here are the IR, ^{13}C NMR, and ^1H NMR spectra for an unknown with the formula $\text{C}_6\text{H}_{10}\text{O}_2$. Answer questions on the next page.



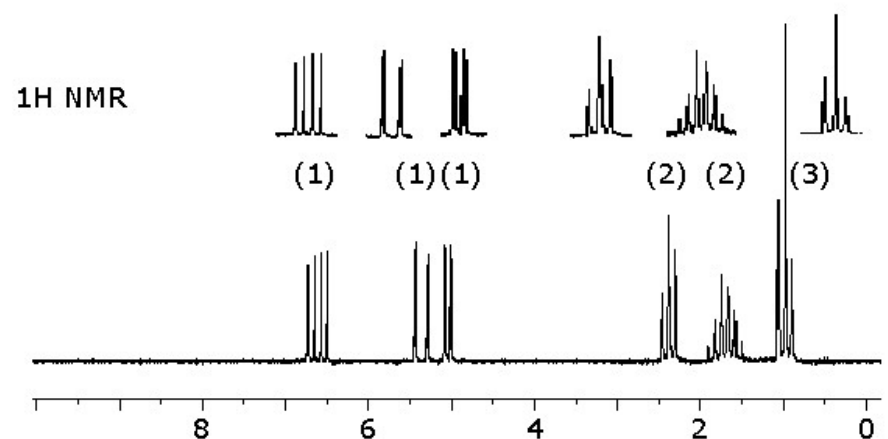
IR spectrum

3500 3000 2000 1500 1000



^{13}C NMR

200 150 100 50 0



^1H NMR

(1) (1) (1) (2) (2) (3)

C

Name: _____

5 continued. (40 points) These questions all refer to the spectra on the previous page.

i) How many degrees of unsaturation are in this compound?

2

j) Is there symmetry in this compound?

no

k) In the IR, what does the signal at about 1740 suggest?

a C=O double bond

l) In the ^{13}C NMR, what does the chemical shift of the signal at about 105 suggest?

an sp^2 C

m) In the ^1H NMR, what does the chemical shift of the signal at about 5.2 suggest?

H on an alkene

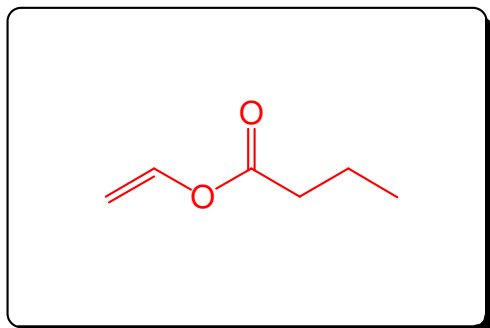
n) In the ^1H NMR, what does the integration of the signal at about 2.3 suggest?

This is probably a CH_2

o) In the ^1H NMR, what does the splitting pattern of the signal at about 1.0 suggest?

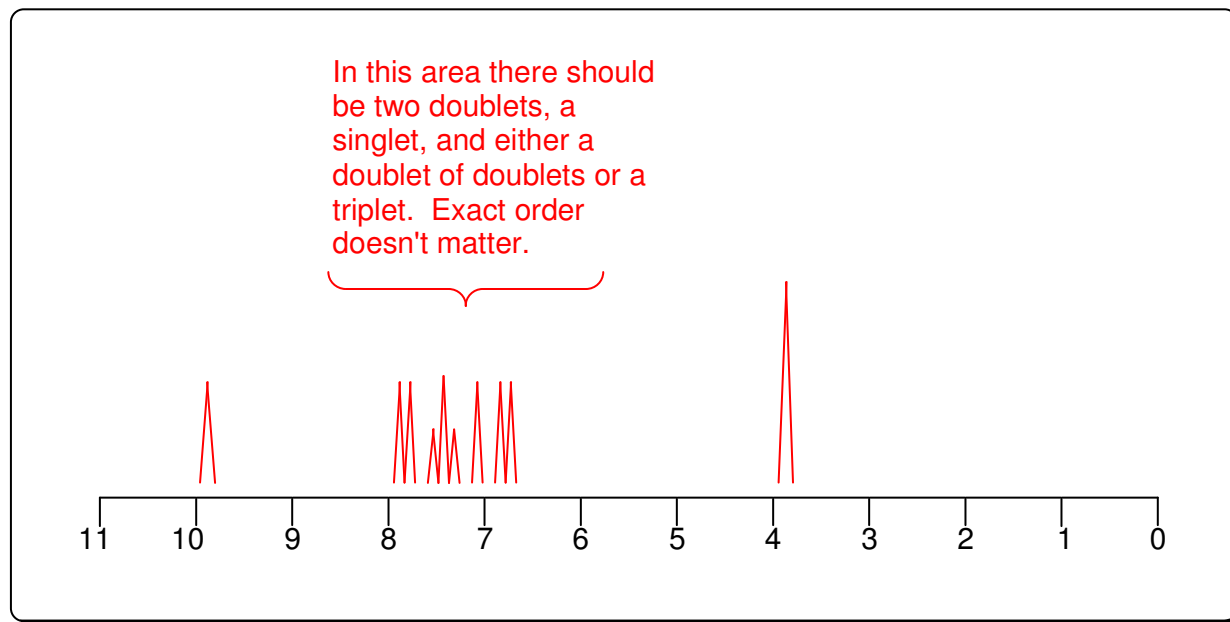
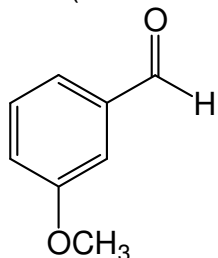
This group is next to two hydrogens.

p) What is the structure of this unknown?

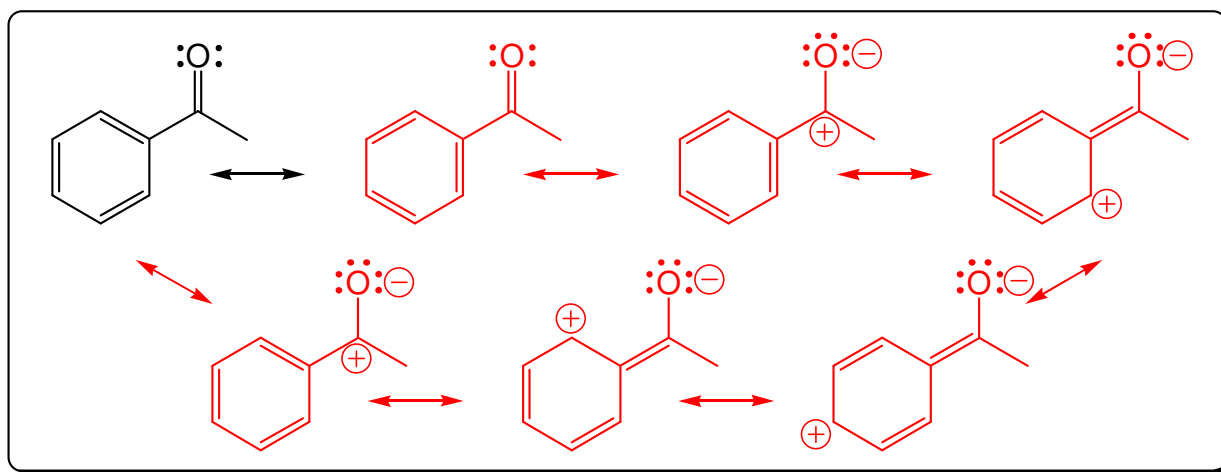


Name: _____

6. (30 points) Draw what you would expect to see in the ^1H NMR of this compound. Your drawing should clearly show the number of signals, their approximate chemical shift (within 1 PPM) and the expected splitting pattern.

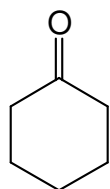


7. (15 points) Draw the important resonance structures for this compound.

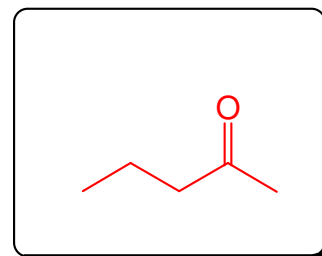
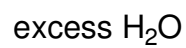
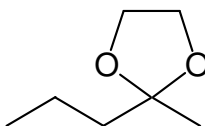
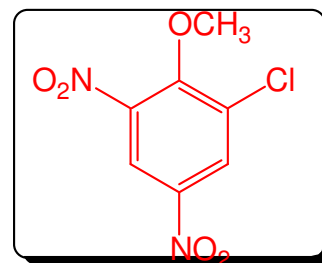
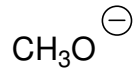
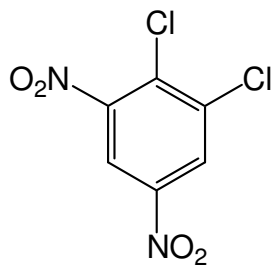
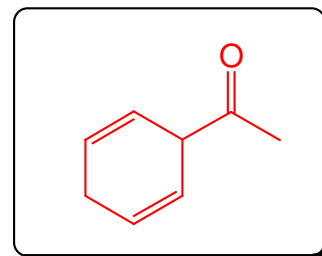
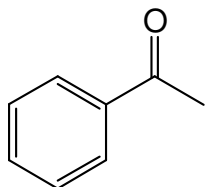
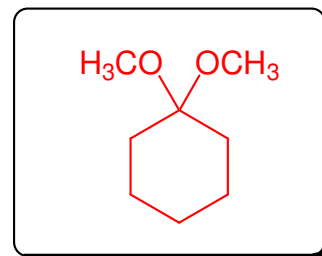
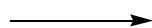
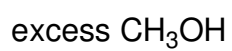
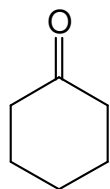
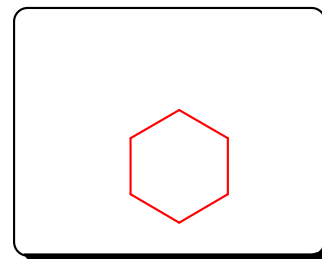


Name: _____

8. (50 points) Predict the major organic product or products for the following reactions.



heat



Name: _____

9. (40 points) Please draw a reasonable arrow-pushing mechanism for the following reaction.

