Last Name

First Name

| Page | Possible Points | Score |
|---|---|---|
| 1 | 50 | |
| 2 | 20 | |
| 3 | 20 | |
| 4 | 25 | |
| 5 | 25 | |
| 6 | 30 | |
| 7 | 30 | |
| 8 | 35 | |
| 9 | 20 | |
| 10 | 20 | |
| 11 | 15 | |
| 12 | 5 | |
| 13 | 15 | |
| 14 | 30 | |
| 15 | 40 | |
| Total | 380 | |

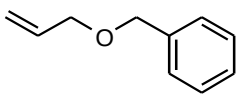
**The exam must be written in ink**.
You have 3 hours to complete the exam.

Email: _____

CHEM 610B
Final Exam
Spring 2000
Instructor: Dr. Pagenkopf

NAME:_____ Final/610B/Pagenkopf

Question 1 (50 points). Roadmap. Provide the products from each reaction in the box. The molecular formula of each product is provided for you. *Clue*: a by-product in the reaction from box B to C is toluene (shown above box C).

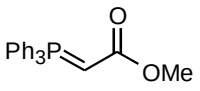


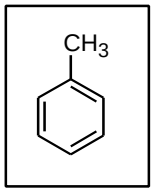
$C_{10}H_{12}O$

1) $OsO_4$

2) $HIO_4$

$C_9H_{10}O_2$





+

**C**

$C_5H_{10}O_3$

$H_2$, Pd/C

**B**

$C_{12}H_{14}O_3$

$H^+$, mild heat

1) MeMgBr (excess)

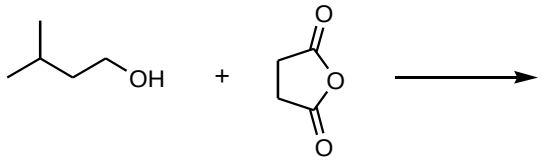
2) then work-up

$C_4H_6O_2$

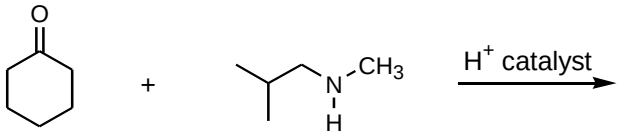
$C_6H_{14}O_2$

Question 2 (90 points). Reactions. Draw the major product for each of the following reactions.

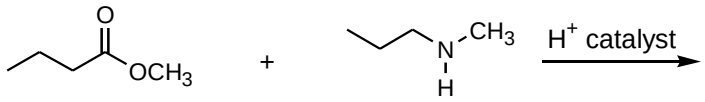
a)



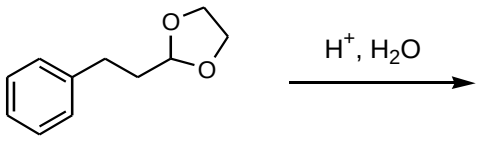

b)



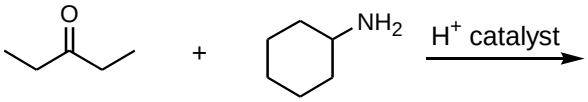

c)



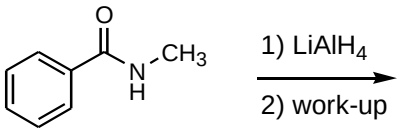

d)



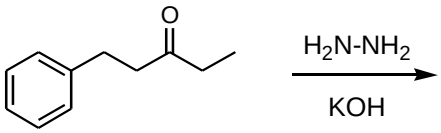
e)


O
+
NH2
H+ catalyst

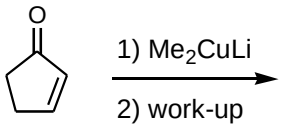
f)


O
N
H
CH3
1) LiAlH4
2) work-up

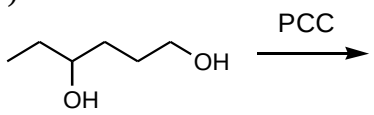
g)


O
H2N-NH2
KOH

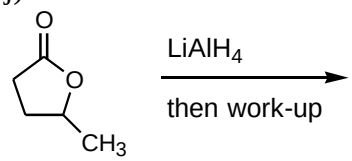
h)


O
1) Me2CuLi
2) work-up

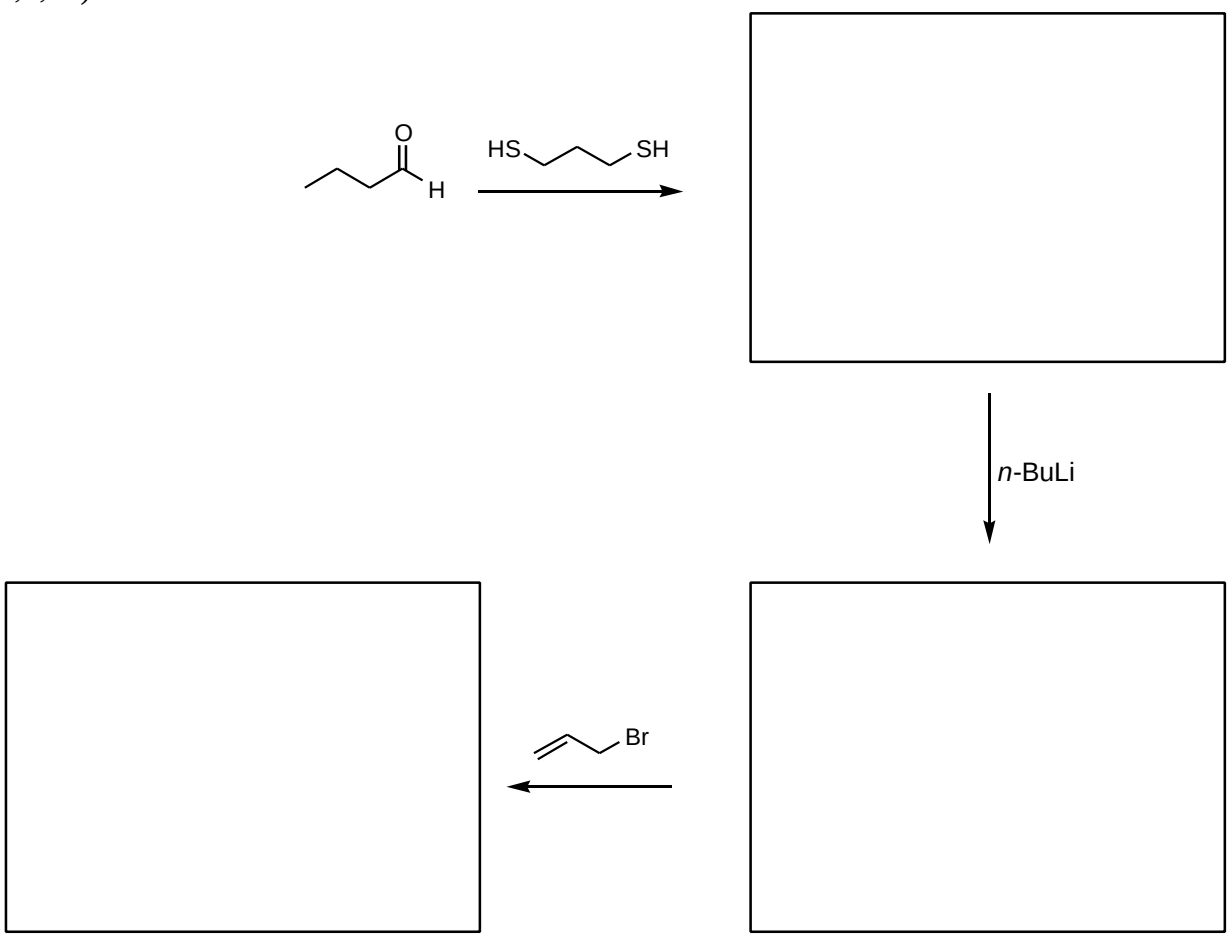
i)



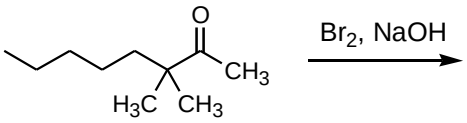

j)



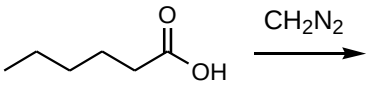

k, l, m)



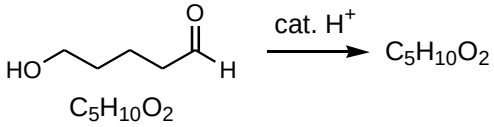
n)



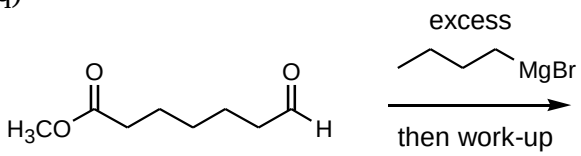

o)



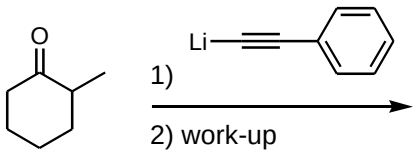

p) hint: product is a hemi-acetal




q)

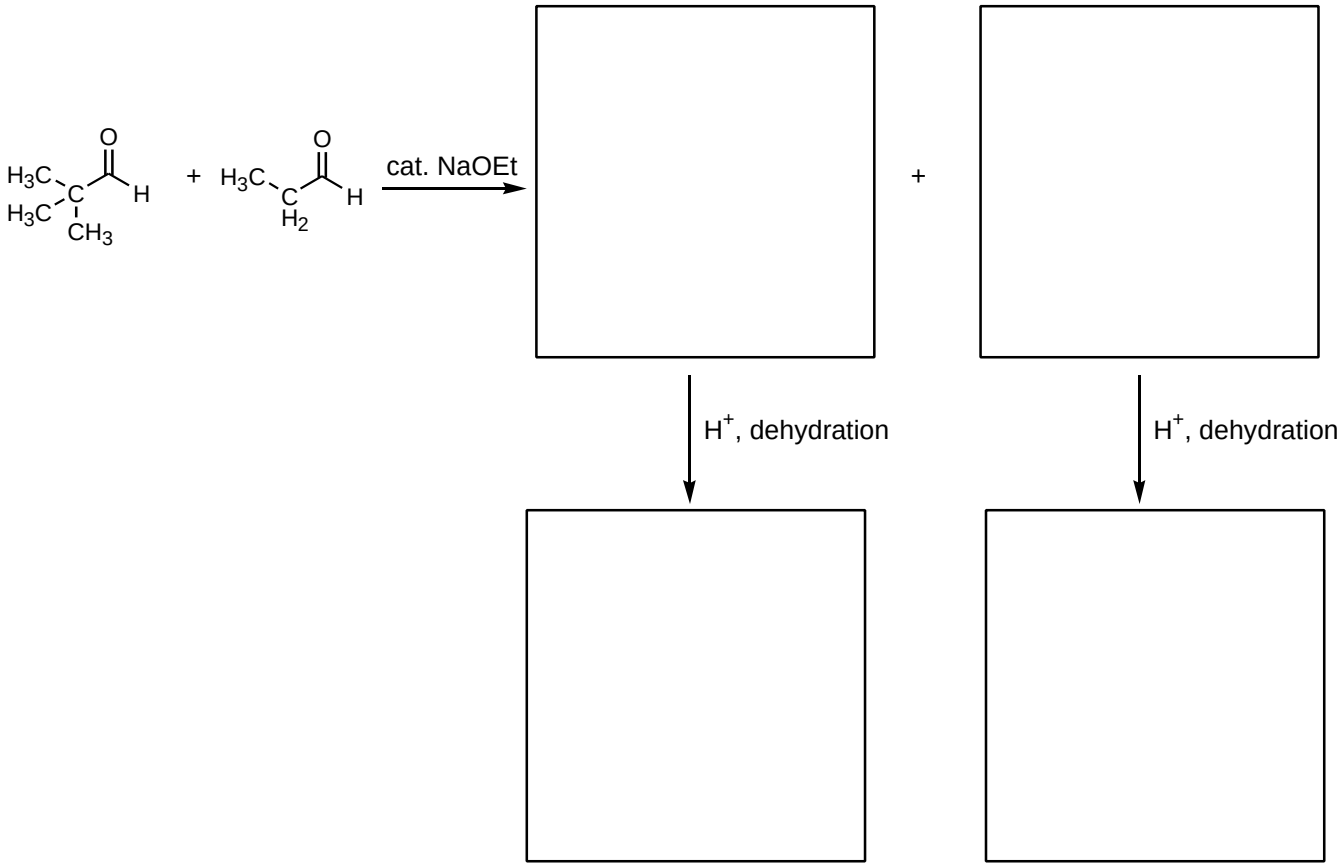



r)



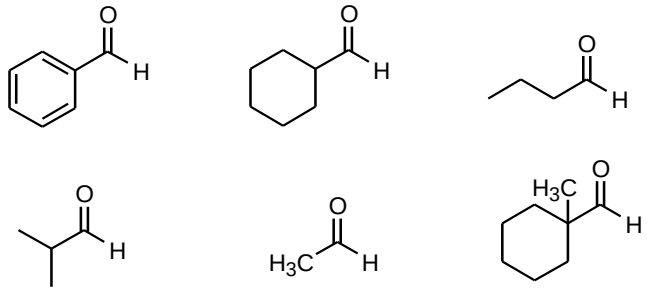
Question 3 (30 points). Aldol Reactions.

a) Show the products of the following aldol condensations. For each question first show one β-hydroxy aldehyde in each of the two boxes, then show the α,β-unsaturated product from dehydration in the next boxes.



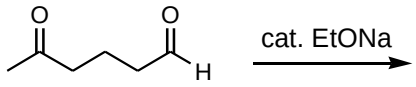

b) How many different aldol condensation products (as β-hydroxy aldehydes) are possible from the following mix of aldehydes, even if expected to be a minor product? Circle your answer.

a) 6
b) 12
c) 17
d) 24
e) 28
f) 35
g) 36
h) 128
i) 46,656

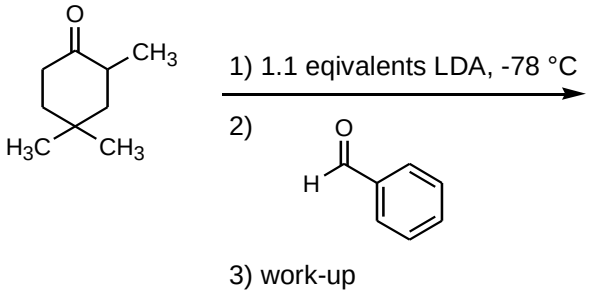


Aldol Reactions continued.

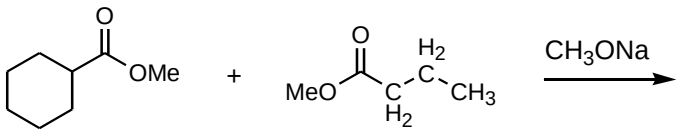
c) (20 points) The following molecule undergoes a self (or intramolecular) aldol condensation followed by elimination (or dehydration) when treated with catalytic EtONa. Show the intramolecular aldol product after dehydration.



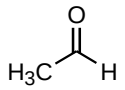

d) (10 points) What is the major aldol product formed under the conditions indicated? You may assume that the ketone only reacts with benzaldehyde and not itself. *reminder*: LDA = $LiN(CHCH_3)_2$



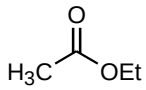
Question 4 (35 points). Claisen Condensations. Show the four products from the following Claisen condensation. Also, show a detailed mechanism for the formation of one of the four products.



Question 5 (20 points). Brief Essay. Explain why an aldol reaction needs only catalytic amounts of EtONa but a Claisen reaction (typically) requires a full equivalent. Your explanation must use specific chemical structures and address the relative acid and base strengths of starting materials, intermediates and products. Show structures and comment on the stabilities of the enolates involved, equilibrium in the reactions and on mechanisms. However, the emphasis should be on relative acid/base strengths and equilibrium (show the equilibrium equations), but specific pKa's are not necessary. To illustrate your answer, use acetaldehyde for the aldol and ethyl acetate for the Claisen.

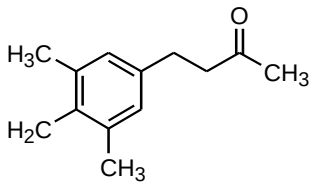


acetaldehyde

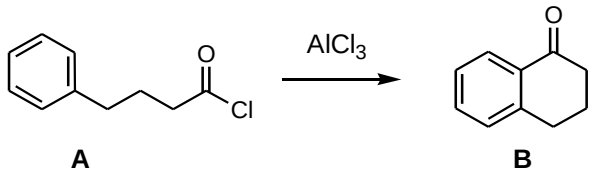


ethyl acetate

Question 6 (20 points). Show how to synthesize the following compound using either the malonic ester synthesis or the acetoacetic ester synthesis by providing the necessary reagents and conditions.



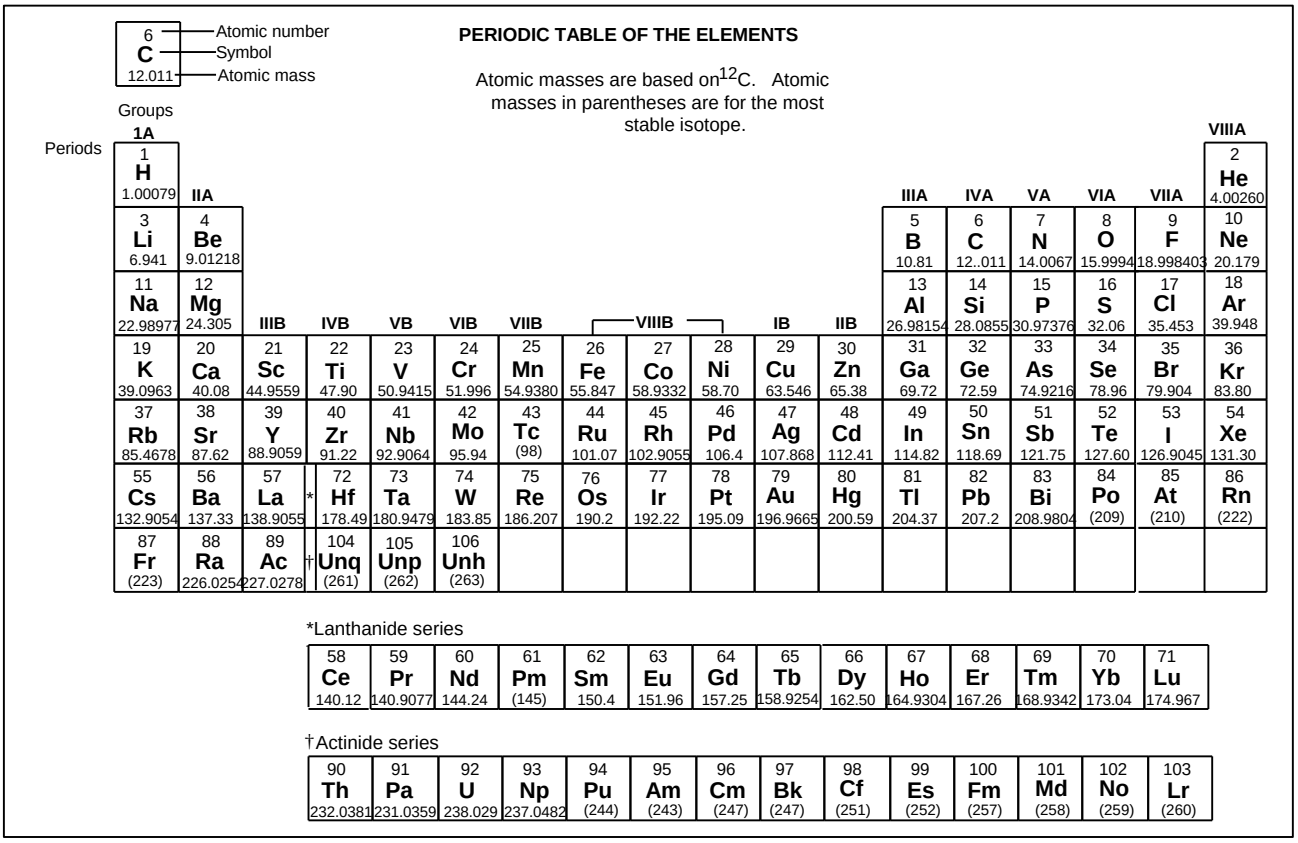
Question 7 (15 points). Mechanisms. When **A** is treated with aluminum trichloride, **B** is formed in high yield. Propose a mechanism for this transformation.




**A** **B**

Question 8. NMR.

a) 5 points. A student was asked to make a Grignard reagent from *para*-bromotoluene and then treat this with ethylene oxide. When the student was almost finished, he noticed that there were two bottles of starting material, one labeled *meta* and the other labeled *para*. However, he didn't know which bottle he had used! The student started to panic, but you told him not to worry because you could help. After looking at the NMR of his reaction product (shown below) do you think he used the correct bottle of *para* starting material? YES or NO?



NAME:_____ /610B/Pagenkopf

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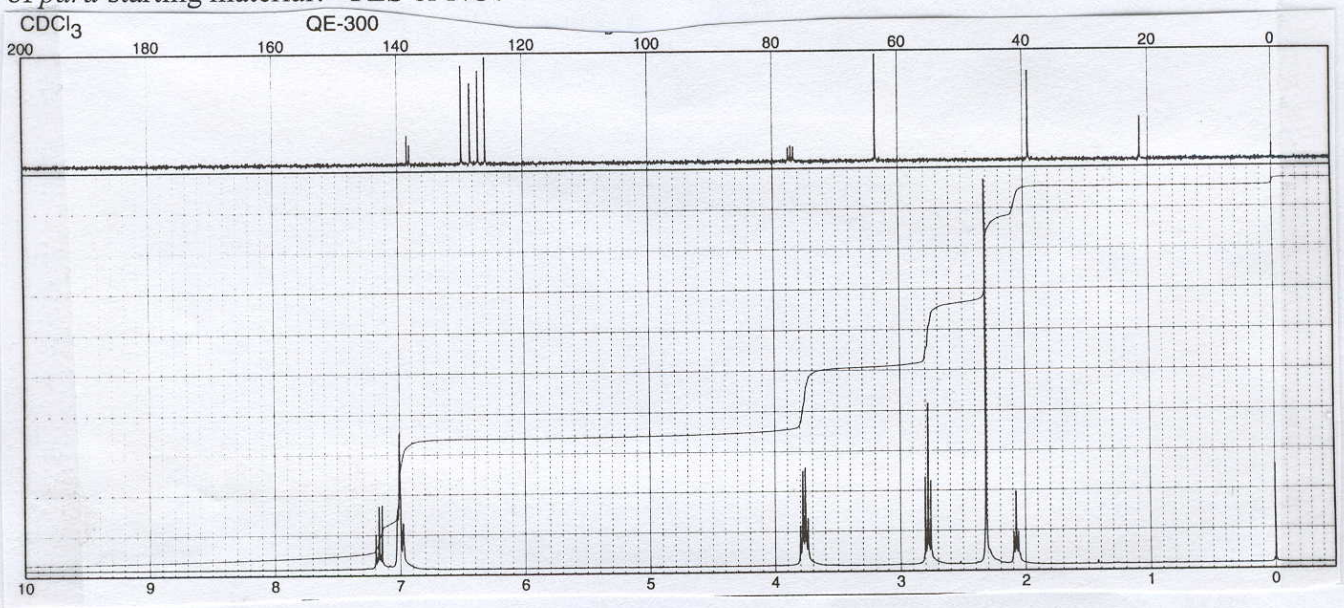


**PERIODIC TABLE OF THE ELEMENTS**

Atomic masses are based on $^{12}C$. Atomic masses in parentheses are for the most stable isotope.

6 C 12.011 — Atomic number, Symbol, Atomic mass

| Periods | Groups 1A | IIA | IIIB | IVB | VB | VIB | VIIB | VIIIB | | | IB | IIB | IIIA | IVA | VA | VIA | VIIA | VIIIA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 H 1.00079 | | | | | | | | | | | | | | | | | 2 He 4.00260 |
| | 3 Li 6.941 | 4 Be 9.01218 | | | | | | | | | | | 5 B 10.81 | 6 C 12..011 | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.998403 | 10 Ne 20.179 |
| | 11 Na 22.98977 | 12 Mg 24.305 | | | | | | | | | | | 13 Al 26.98154 | 14 Si 28.0855 | 15 P 30.97376 | 16 S 32.06 | 17 Cl 35.453 | 18 Ar 39.948 |
| | 19 K 39.0963 | 20 Ca 40.08 | 21 Sc 44.9559 | 22 Ti 47.90 | 23 V 50.9415 | 24 Cr 51.996 | 25 Mn 54.9380 | 26 Fe 55.847 | 27 Co 58.9332 | 28 Ni 58.70 | 29 Cu 63.546 | 30 Zn 65.38 | 31 Ga 69.72 | 32 Ge 72.59 | 33 As 74.9216 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.80 |
| | 37 Rb 85.4678 | 38 Sr 87.62 | 39 Y 88.9059 | 40 Zr 91.22 | 41 Nb 92.9064 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.9055 | 46 Pd 106.4 | 47 Ag 107.868 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.69 | 51 Sb 121.75 | 52 Te 127.60 | 53 I 126.9045 | 54 Xe 131.30 |
| | 55 Cs 132.9054 | 56 Ba 137.33 | 57 La 138.9055 | * 72 Hf 178.49 | 73 Ta 180.9479 | 74 W 183.85 | 75 Re 186.207 | 76 Os 190.2 | 77 Ir 192.22 | 78 Pt 195.09 | 79 Au 196.9665 | 80 Hg 200.59 | 81 Tl 204.37 | 82 Pb 207.2 | 83 Bi 208.9804 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| | 87 Fr (223) | 88 Ra 226.0254 | 89 Ac 227.0278 | † 104 Unq (261) | 105 Unp (262) | 106 Unh (263) | | | | | | | | | | | | |

*Lanthanide series

| 58 Ce 140.12 | 59 Pr 140.9077 | 60 Nd 144.24 | 61 Pm (145) | 62 Sm 150.4 | 63 Eu 151.96 | 64 Gd 157.25 | 65 Tb 158.9254 | 66 Dy 162.50 | 67 Ho 164.9304 | 68 Er 167.26 | 69 Tm 168.9342 | 70 Yb 173.04 | 71 Lu 174.967 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

†Actinide series

| 90 Th 232.0381 | 91 Pa 231.0359 | 92 U 238.029 | 93 Np 237.0482 | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) | 103 Lr (260) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

NMR. Continued.

b) 15 points. Compound **I**, $C_{11}H_{14}O_2$, is insoluble in water, aqueous acid, and aqueous $NaHCO_3$ but dissolves readily in 10% $Na_2CO_3$ and 10% NaOH. When these alkaline solutions are acidified with 10% HCl, compound **I** is recovered unchanged. Given this information and its $^1$H-NMR spectrum, deduce the structure of compound **I** and draw your structure in the box at the bottom of this page.

NAME:_____ 610B/Pagenkopf

NMR. Continued.

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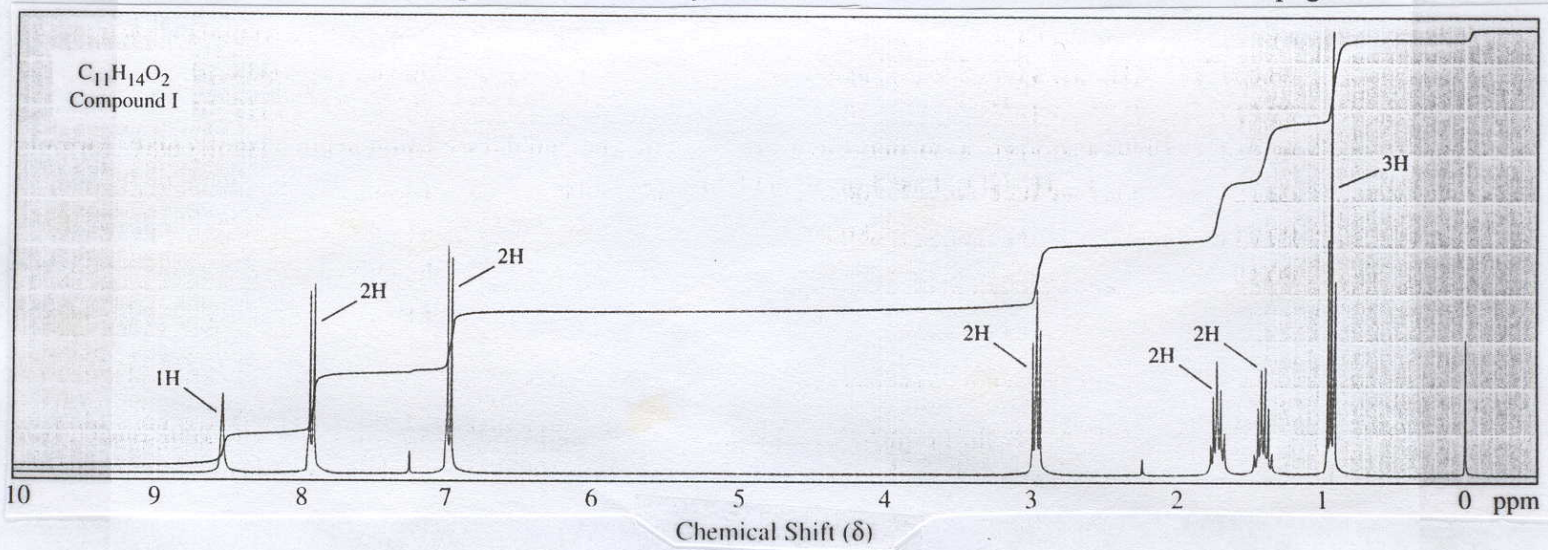
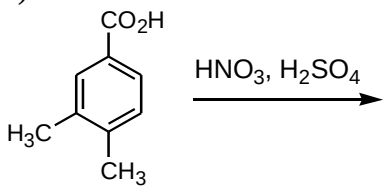
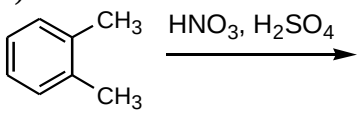


Question 9 (30 points). Electrophilic aromatic substitution reactions. Draw the major product expected from each of the following reactions. For each nitration reaction, add only one nitro group to the aromatic ring.

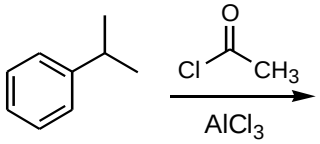
a)



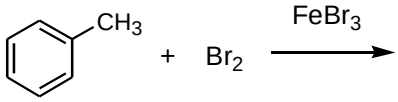

b)



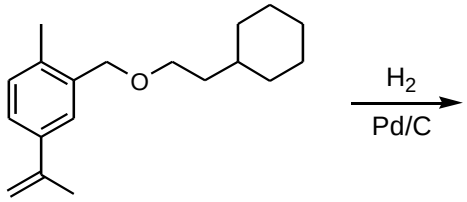

c)



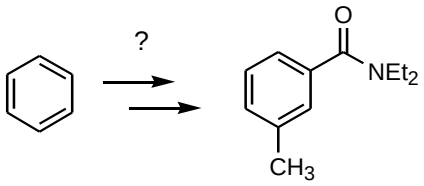

d)




e) Two Products



Question 10 (40 points). Synthesis. DEET, *N*,*N*-diethyl-*m*-toluamide, is the active ingredient in several common insect repellents. Propose a synthesis of DEET from benzene. There are numerous viable synthetic routes to DEET and it may help to think about the problem retrosynthetically. For example, if the last transformation(s) you propose is preparation of the amide from another carboxylic acid derivative, then the problem may simplify considerably. With two functional groups that we know how to attach to benzene, all we need to do is select a sequence that ensures their *meta* relationship.






*End of exam!* Have a great summer and good best wishes for your future!