Chemistry 3371: Organic Chemistry

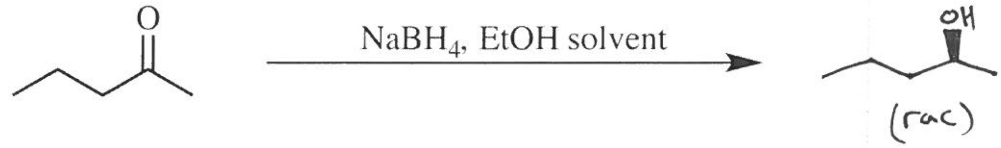
Instructor: Hubert Yin/TA: Adam Csakai

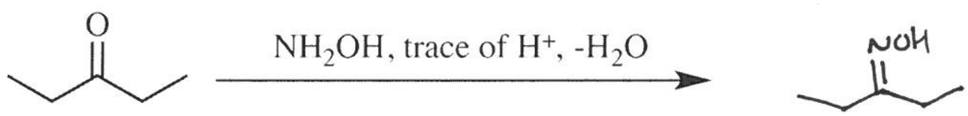
Tuesday: Mar. 8 @ **7:00 - 9:00 PM** /2nd Exam

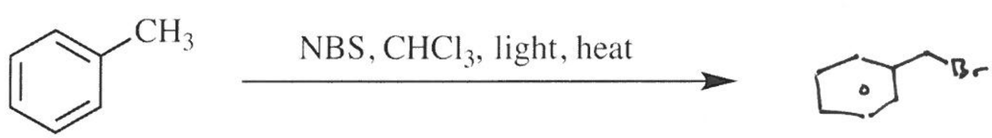
Name: Key (please print, 1 pt)

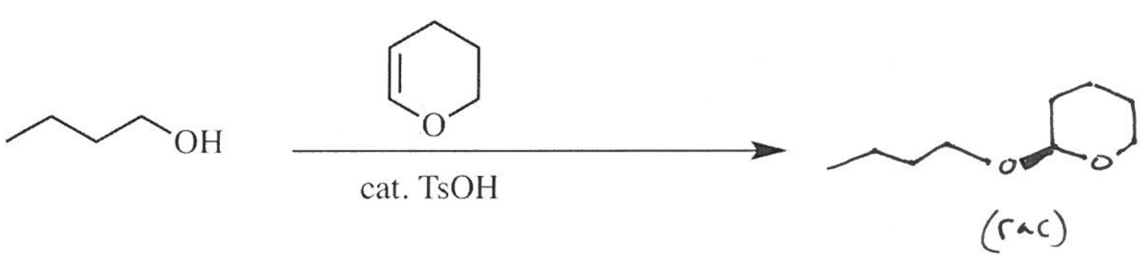
Page	Possible Points	Score
1	1	
2	12	
3	8	
4	8	
5	10	
6	15	
7	16	
8	10	
9	10	
11	10	
12	Appendix: Periodic Table, common NMR, IR absorption	
TOTAL	100	

1. Give the single major product of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac" (3 pts each)

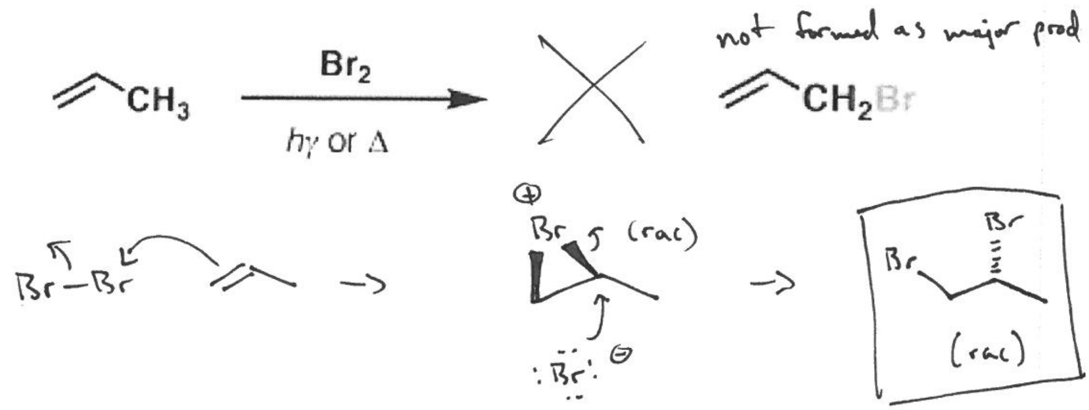
a) 

b) 

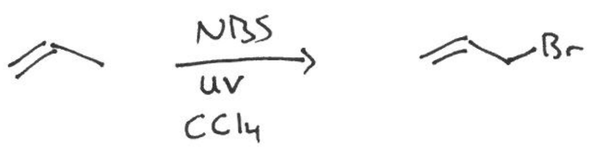
c) 

d) 

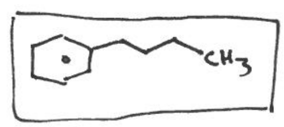
2. (8 pts) Adam plans to carry out an allylic bromination as shown below? Do you think that he will get the desired product? If not, what will be major actual product? Also, please suggest a different method to avoid this?

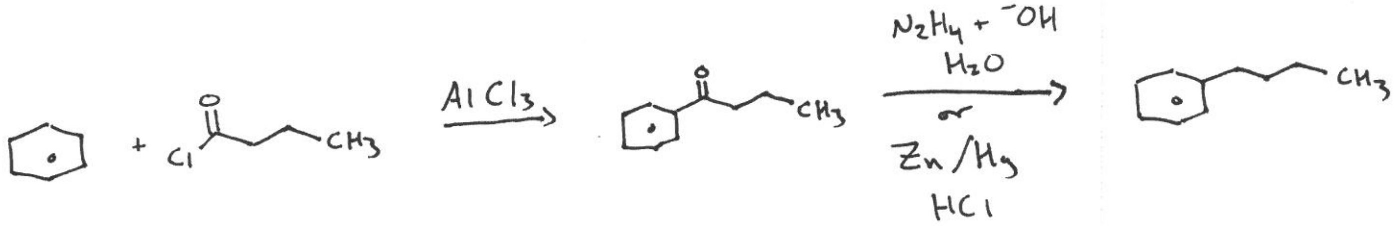


Better Conditions:

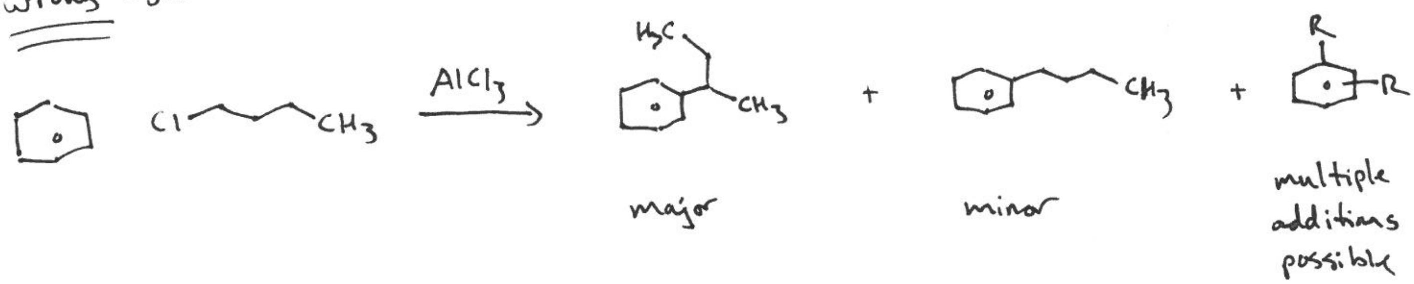


3. (8 pts) Outline a synthesis of butylbenzene from benzene and any other reagents.

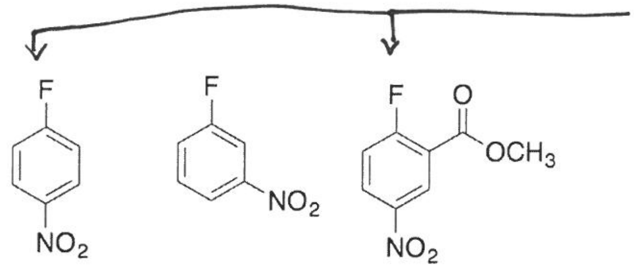




wrong synthetic plan:

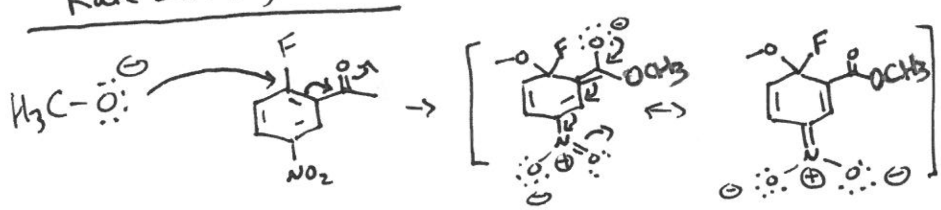


4. (10 pts) Arrange the three following compounds in according to their relative rate of reaction with potassium methoxide in methanol. Justify the order.

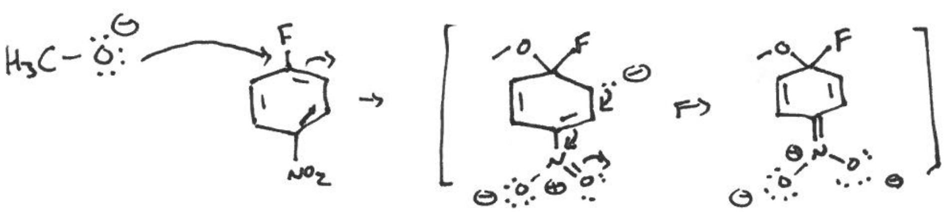


ortho + para withdrawing groups also allow for several other resonance structures (not drawn) that place a lone pair w/ negative charge on carbons ortho + para to F

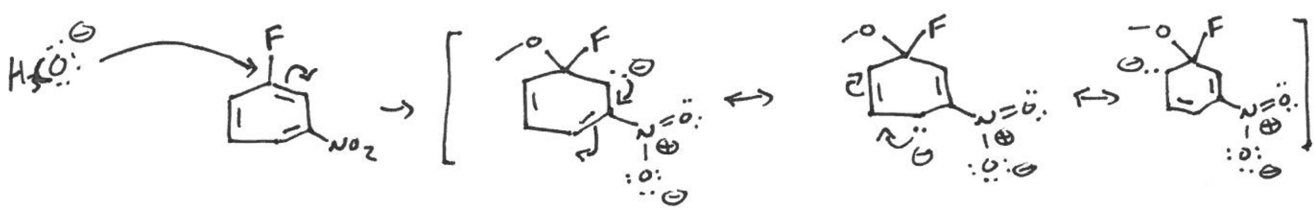
Rate Limiting Step



electron withdrawing groups at the ortho + para positions allow for resonance structures with negative charge on oxygen atoms } Fastest Rate



Same reasoning, but only one group that can accept electrons at the para position (none @ ortho) } Second Fastest Rate

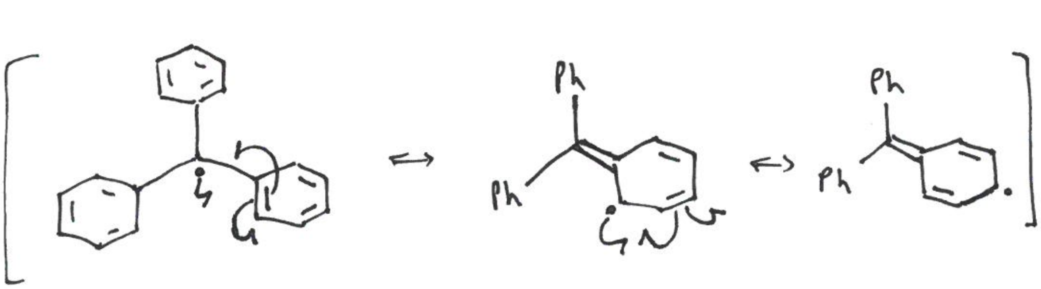


} Slowest Rate

Electron withdrawing group on meta position cannot take negative charge in any resonance structure. All structures possible place negative charge on carbon atoms → high energy

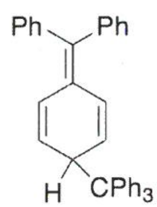
5. (15 pts) Around 1900, Moses Gomberg, a pioneer in free- radical chemistry, prepared the triphenylmethyl radical, Ph_3C□, sometimes called the trityl radical.

(a) Explain why the trityl radical is an unusually stable radical.

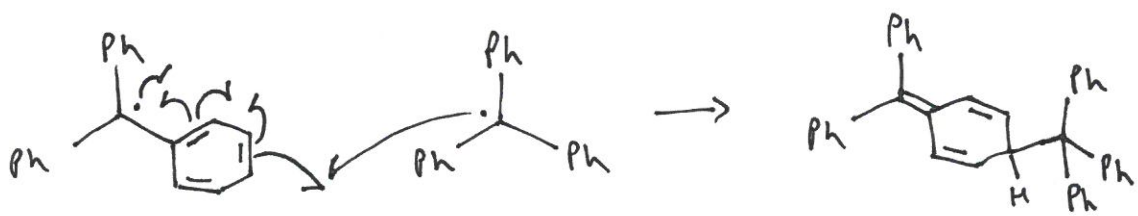


radical character is spread out across several carbons (i.e. delocalized)

(b) The trityl radical is known to exist in equilibrium with a dimer that, for many years, was assumed to be hexaphenylethane, $Ph_3C\text{-}CPh_3$. In 1968, the structure of this dimer was investigated and found not to be hexaphenylethane, but rather the following compound. Using the fishhook notation, show how this compound is found from two trityl radicals, and explain why this compound is formed instead of hexaphenylethane.



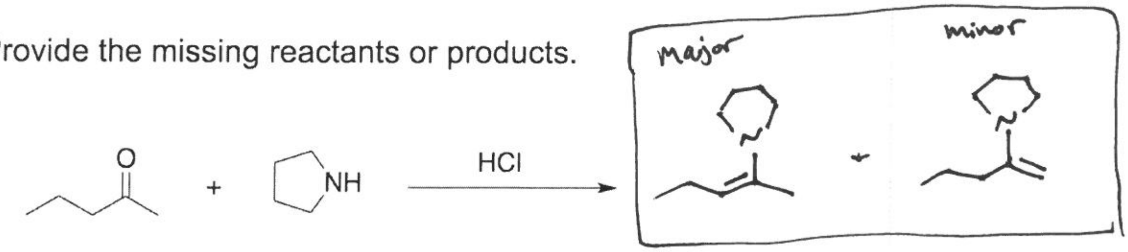
dimer of trityl radical



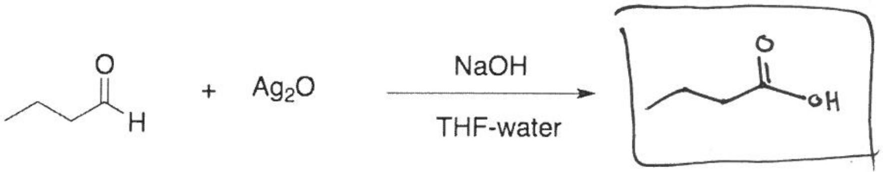
Starting from the best resonance structure x2

6. (16 pts) Provide the missing reactants or products.

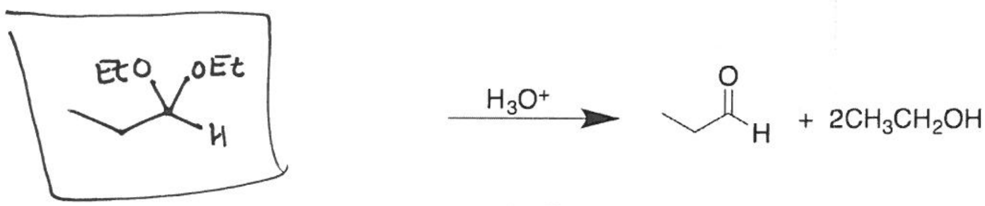
(a)



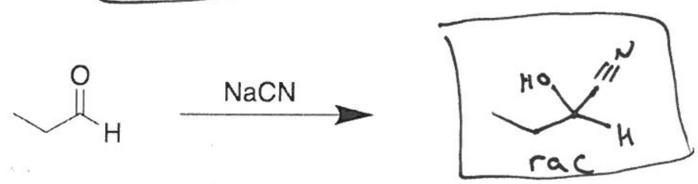
(b)



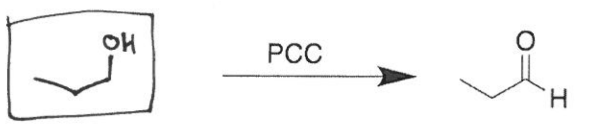
(c)



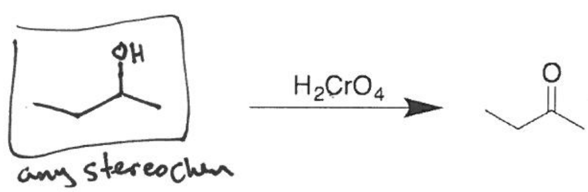
(d)



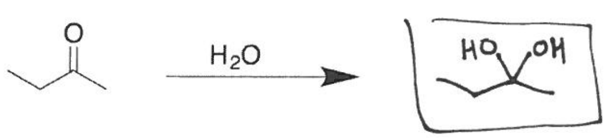
(e)



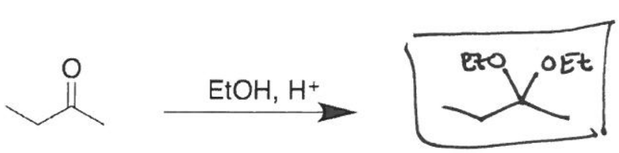
(f)



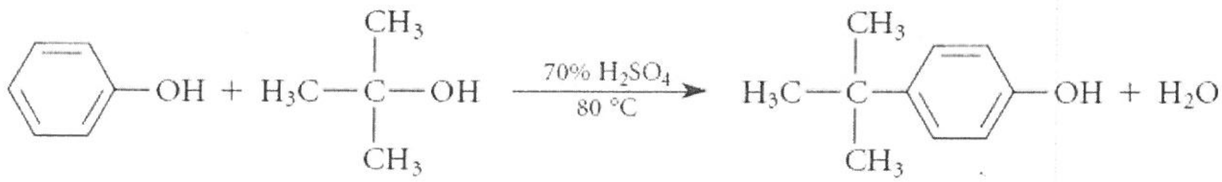
(g)



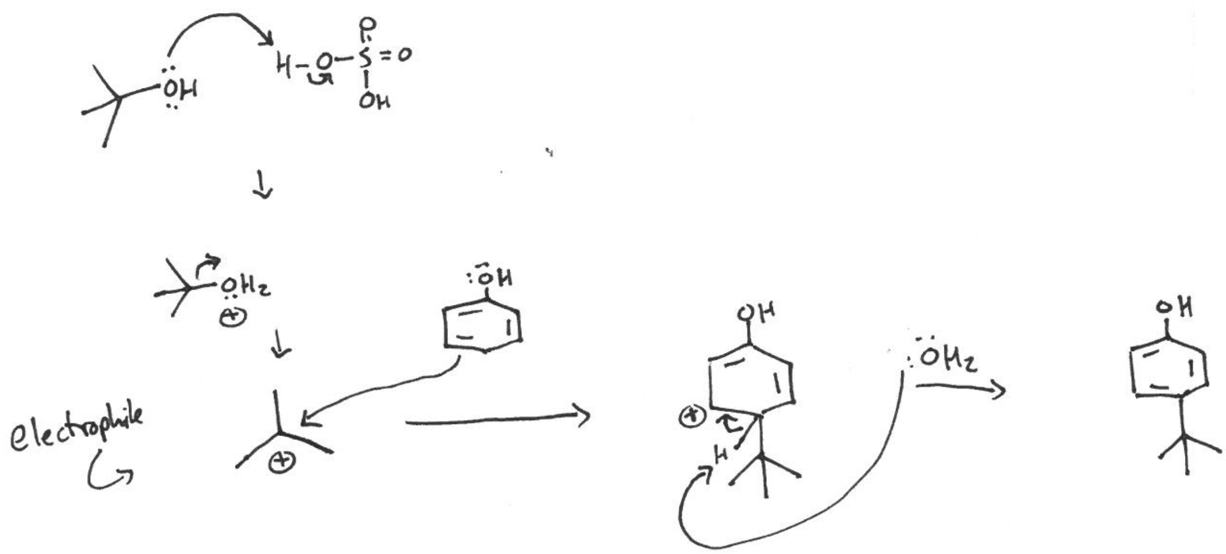
(h)



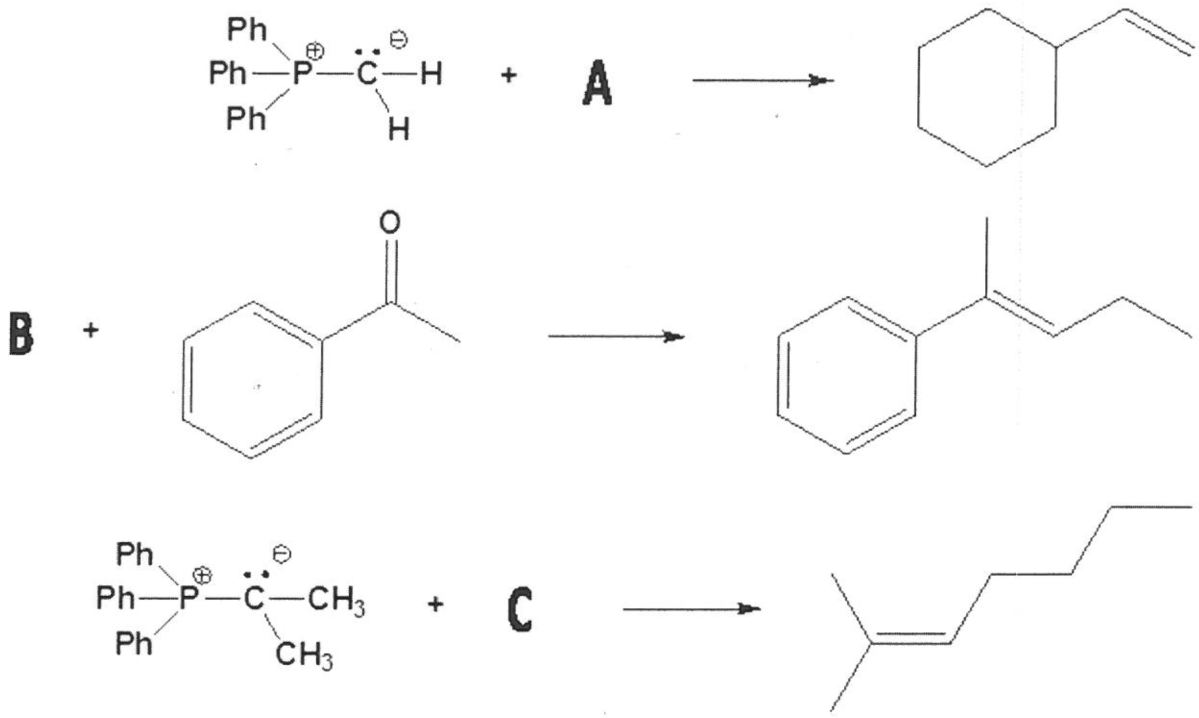
7. (10 pts) Give a curved-arrow mechanism for the reaction below. Be sure to identify the electrophilic species in the reaction and to show how it is formed.

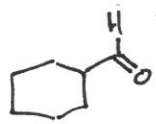


p-tert-butylphenol
(80% yield)

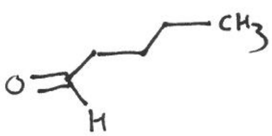


9. (10 pts) Please indicate the starting material required to produce the product.



A) 

B) 

C) 

$\frac{2(7)+2-10}{2}$

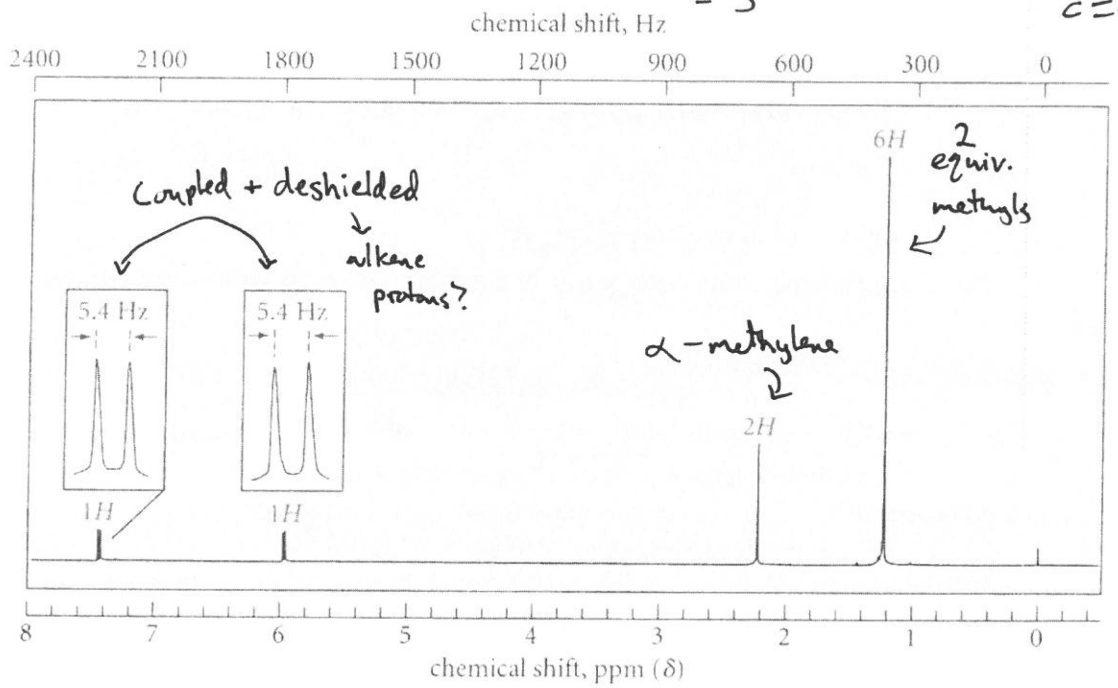
19.67

10. (10 pts) Identify the compound $C_7H_{10}O$ that has an IR absorption at 1703 cm^{-1} and the proton NMR spectrum shown below.

degree unsat = 3

C=O (but no CHO

present = ketone)

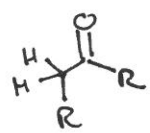


degree unsat — molecular formula

IR@1703 cm^{-1} →

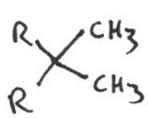
↓

α-methylene protons @ 2.1ppm →



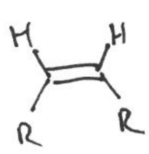
→ 1 → C_2H_2O

2 equivalent CH_3's @ 1.1 ppm, not coupled to anything (isolated) →



→ C_5H_8O

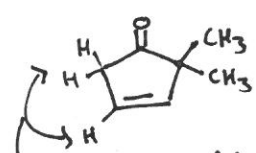
alkene protons only coupled to each other (isolated alkene) →



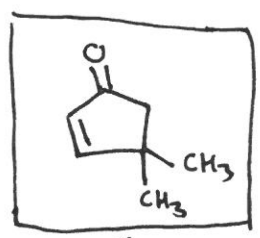
→ (2) → $C_7H_{10}O$

only 2 double bonds (need 1 more or 1 ring)

wrong isomer: (but close)



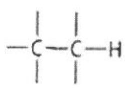
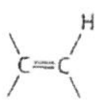
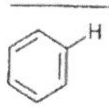
coupling would be observed



Sum of 3 components (functional groups) gives complete formula, but incomplete degree of sat. number. I.E. must make a ring

Appendix

hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

Group	Chemical shift, ppm
	0.7–1.5
	4.6–5.7
—O—H	varies with solvent and with acidity of O—H
—C≡C—H	1.7–2.5
	6.5–8.5

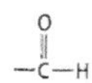
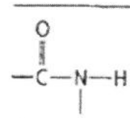
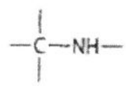
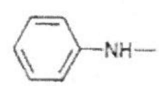
Group	Chemical shift, ppm
	9–11
	7.5–9.5
	0.5–1.5
	2.5–3.5

TABLE 12.1 Regions of the Infrared Spectrum

Wavenumber range, cm^{-1}	Type of absorptions	Name of region
3400–2800	O—H, N—H, C—H stretching	Functional group
2250–2100	C≡N, C≡C stretching	
1850–1600	C=O, C=N, C=C stretching	
1600–1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint
1000–600	C—H bending	C—H bending