Practice EXAM 2

Department of Chemistry
University of Vermont

Chem 142/144
Spring 2001
Exam 2

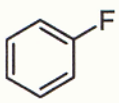
Name:

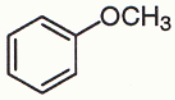
Problem	points (total)	Grader
	_____	_____
	_____	_____
	_____	_____
	_____	_____
	_____	_____
	_____	_____

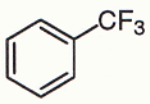
Score:_____

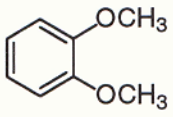
For each question in this section, circle the correct answer. Each problem is worth 3 points.

1. Which of the following would you expect to undergo nitration with HNO_3/H_2SO_4 at the fastest rate?

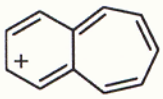


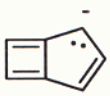


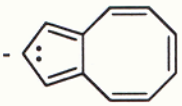


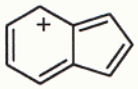


2. Which of the following would you expect to be aromatic?

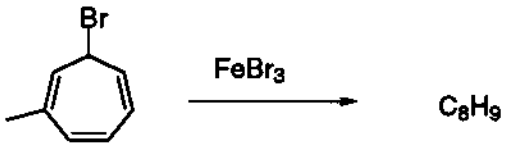






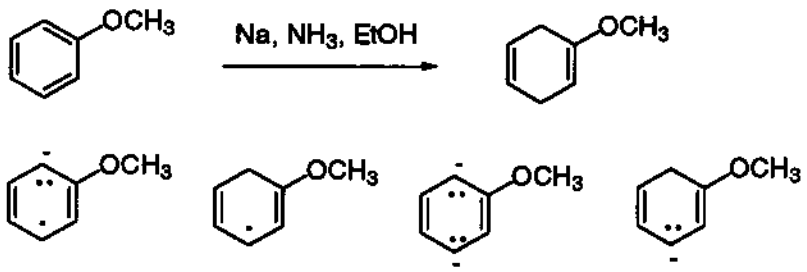


3. How many signals would the ^1H NMR spectrum of the product from the following reaction exhibit?

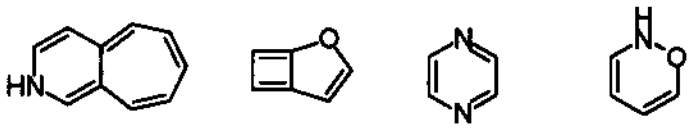


a) 1
b) 2
c) 3
d) 4

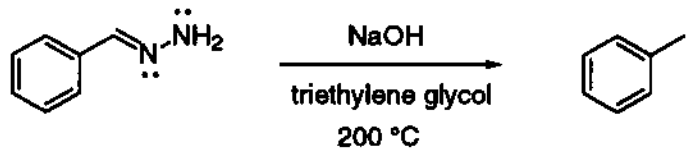
4. Which is not an intermediate in the following transformation?

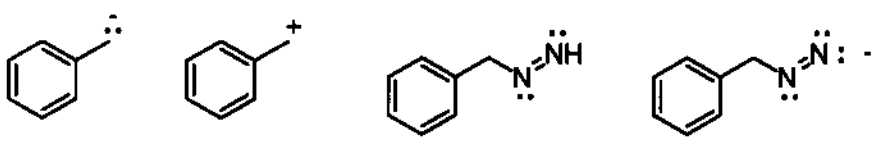


5. Which of the following is aromatic?

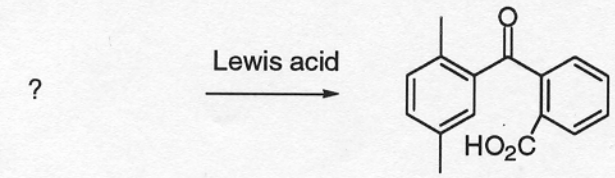


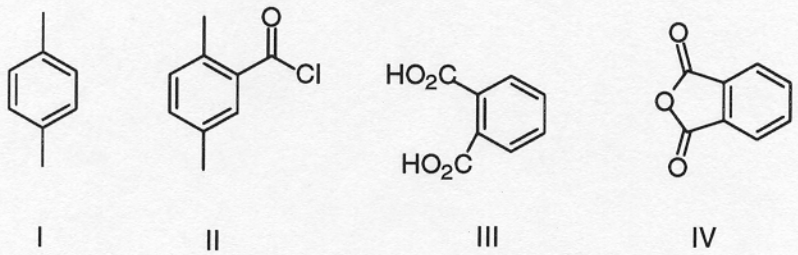
6. Which is not an intermediate in the following transformation?





7. Reaction of which of the following pairs of reagents would constitute the best way to make the product shown in the presence of a Lewis acid?





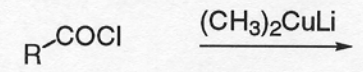
I II III IV

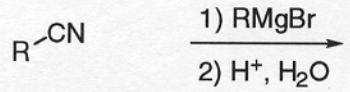
a) I and III
b) I and IV
c) II and III
d) II and IV

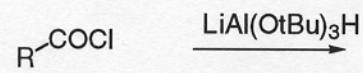
8. Which sequence of steps would accomplish the transformation shown?

a) 1) $KMnO_4$, OH^-, heat, 2) $SOCl_2$, 3) $AlCl_3$, benzene
b) 1) $KMnO_4$, OH^-, heat, 2) $LiAlH_4$, 3) $AlCl_3$, toluene
c) 1) NBS, ROOR, heat, 2) $AlCl_3$, benzene
d) 1) Na, NH_3, EtOH, 2) $SOCl_2$, 3) BF_3, benzene

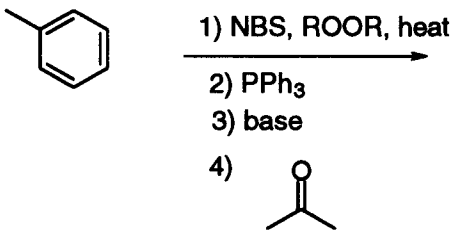
9. Which of the following reactions would not afford a ketone?

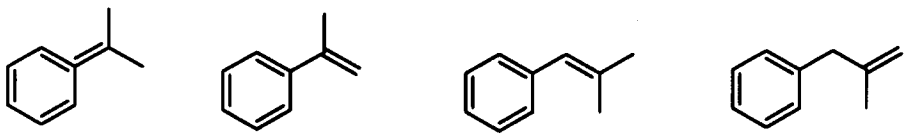




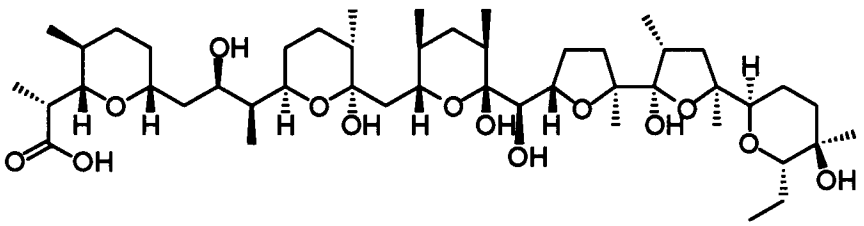


10. What would the product of the following sequence of reactions?



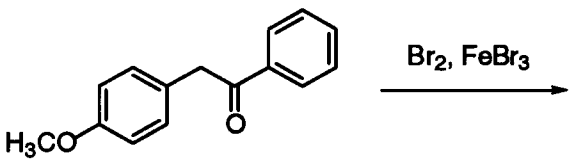


11. The natural product antibiotic X-206 has 3 hemiketal groups. Circle these. **(3 points)**

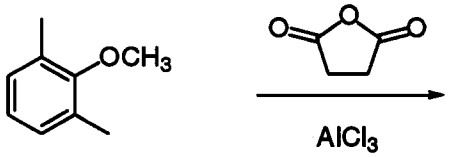


12. Provide the major product expected for each of the following transformations. **(18 points)**

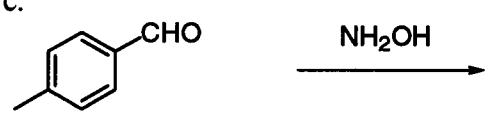
a.



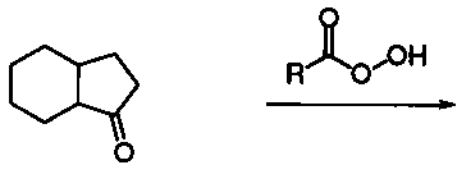
b.



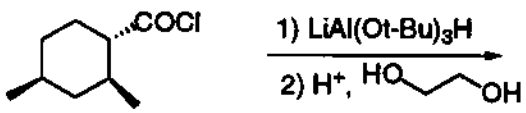
c.



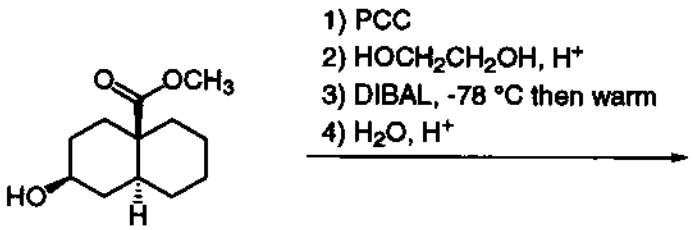
d.



e.

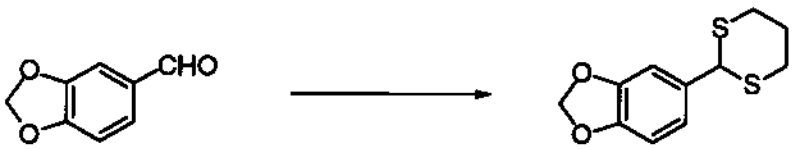


f.



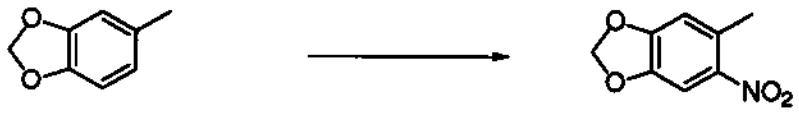
13. Provide the missing reagents necessary to accomplish the following transformations. **(18 points)**

a.



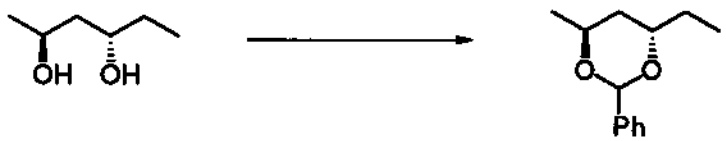
b.

c.



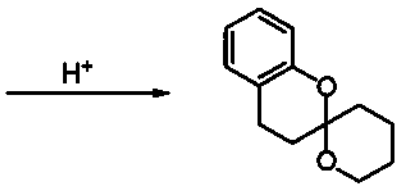
d.

e.

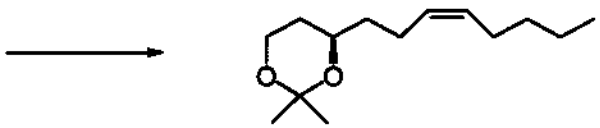


f.

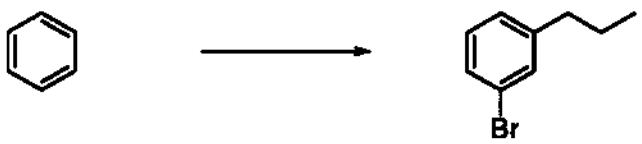
14. Provide the keto-diol that would have undergone ketal formation in the presence of acid to give the product shown. **(4 points)**



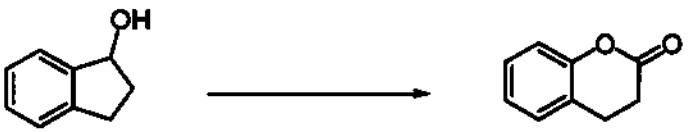
15. Provide two compounds that would react through a Wittig reaction to give the product shown. **(4 points)**



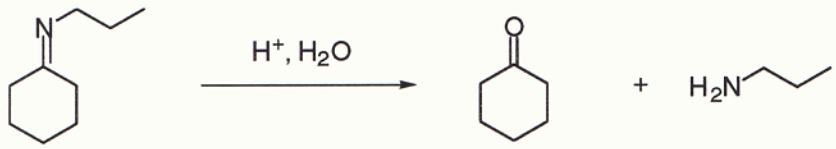
16. Propose a synthesis of the compound shown from benzene. **(6 points)**



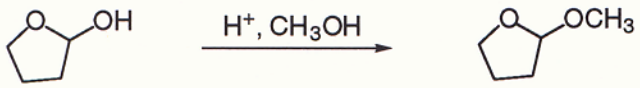
17. Propose a synthesis of the ester shown from the alcohol provided. **(6 points)**



18. Propose a mechanism for the following transformation. **(6 points)**

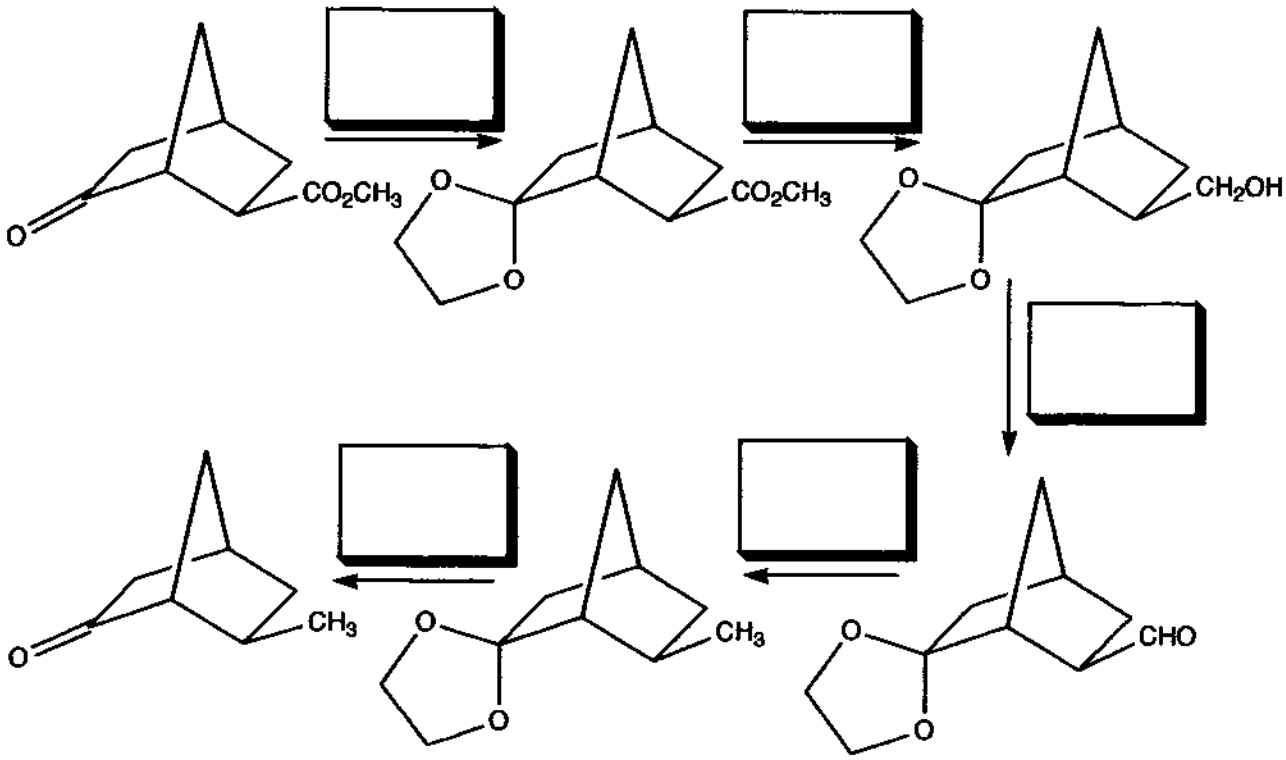


19. Propose a mechanism for the following transformation. **(4 points)**

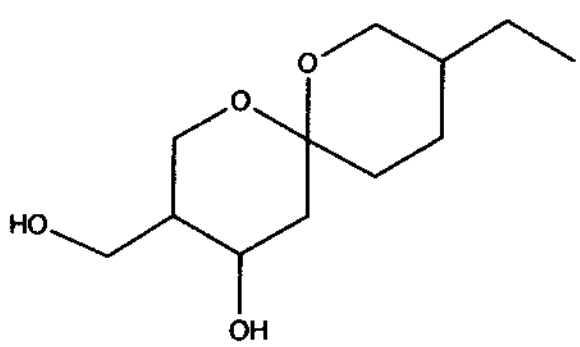


Extra Credit (6 points). Draw three constitutional (structural) isomers with the formula C_6H_6O that are aromatic.

(5) 1. Put reagents on the arrows for the following 5 step synthesis reported in the chemical literature.



(2) 2. Talaromycin A is a toxic substance produced by a fungus growing on poultry house litter in chicken and turkey farms here in Vermont and other New England states. It contains both C=O and alcohol functional groups, but is more stable as a cyclic ketal, shown below. In the box to the right of Talaromycin draw the open chain form of this compound.



Talaromycin

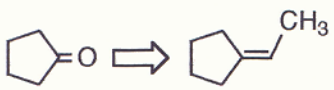
open chain form of Talaromycin

(3) 3. Write the detailed curved arrow mechanism for the formation of the imine produced from the reaction of cyclohexanone and t-butylamine.

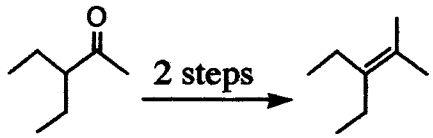
(3) 4. Show an example of the Baeyer-Villiger oxidation.

(3) 5. Show an example of the Wolff-Kishner reduction.

(5) 6. Show how you would carry out the following conversions using any reagents you wish (mechanisms are not necessary)



(5) 6. continued...

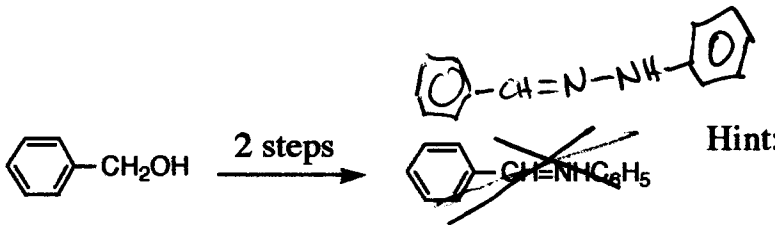


Hint: 1. addition
2. elimination

(5)

Hint: 1. addition
2. hydrolysis

(5)



Hint: 1. oxidation
2. addition

21. The product of $CH_3OH + (CH_3)_2CHCO_2H \xrightarrow{H^+}$ is:

a) $(CH_3)_2CHCO_2CH_3$ b) $(CH_2)_2CHOCH_3$

c) $CH_3CO_2CH(CH_3)_2$ d) methyl valerate

e) methyl caproate

22. Which is most acidic?

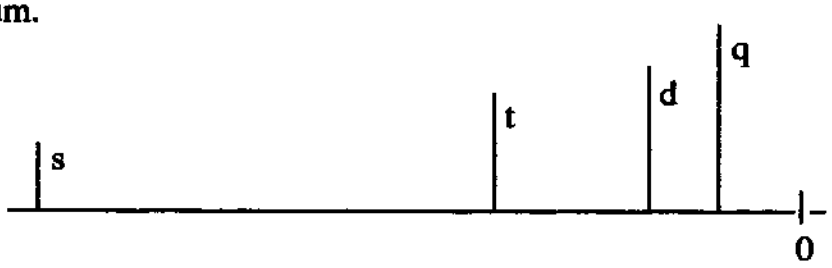
a) C_6H_5OH b) C_2H_5OH c) $C_6H_5CO_2H$ d) $C_2H_5OC_2H_5$ e) C_6H_5CHO

23. A correct name for $CH_3CH_2CO_2C(CH_3)_3$ is:

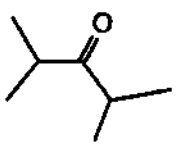
a) isobutyl propanoate b) propyl butanoic ester c) propyl butyrate

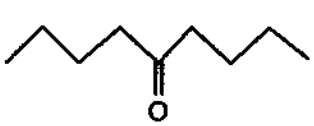
d) tert-butyl propionate e) ethyl-tertbutoxy ketone

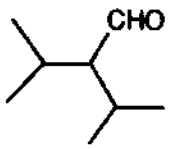
24. Compound A ($C_9H_{18}O$) forms a phenylhydrazone but gives a negative Tollen's test. The IR spectrum shows a strong band near 1710 cm^{-1}. The proton decoupled cmr spectrum is shown below. The letters q,d,t,s near the peaks are the pattern that each indicated peak has in the off resonance decoupled cmr spectrum.

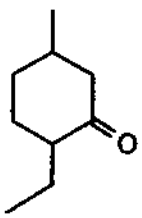


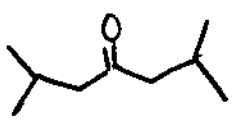
The structure of A is:

a) 

b) 

c) 

d) 

e) 

18. Propanoyl chloride, when reacted with $LiAlH(Ot\text{-}Bu)_3$ at -78°, followed by an aqueous workup, will yield.

a) propanol

b) dipropyl ether

c) t-butyl propyl ether

d) propanal

e) propanoic acid

19. Which is not a synthesis of carboxylic acids?

a) Reaction of alkyl halides with Mg in ether, followed by treatment with carbon dioxide and an aqueous acidic workup.

b) Acid catalyzed hydrolysis of RCN.

c) Reaction of aldehydes with $Ag(NH_3)_2^+$, OH^-

d) Reaction of n-alkyl benzenes with hot alkaline $KMnO_4$.

e) Acid catalyzed hydrolysis of ketals

20. Which is an anhydride?

a) $CH_3CO\text{-}O\text{-}OCH_3$ b) $CH_3OCOOCH_3$ c) $CH_3CO_2COCH_3$

d) CH_3CO_3H e) $CH_3COCH_2CH_2O_2CH_3$

multiple choice are 1 pt. each (10 total points)

15. N-phenyl-N-propylacetamide is:

a) $C_6H_5CH_2CH_2CH_2O_2CCH_2NH_2$

b) $C_6H_5CON(CH_2CH_3)CH_2CH_2CH_3$

c) $C_6H_5CON(CH_2CH_3)_2$

d) $CH_3CON(CH_2CH_3)_2$

e) $CH_3CON(C_6H_5)CH_2CH_2CH_3$

16. The reaction of propanal with $BrCH_2CO_2CH_2CH_3$, Zn and then H_3O^+ will yield:

a) $CH_3CH_2CH(OH)CH_2CO_2CH_2CH_3$

b) $CH_3CH_2OCH_2CO_2CH_2CH_3$

c) $HOCH_2CH_2CH_2CH(OH)CO_2CH_3$

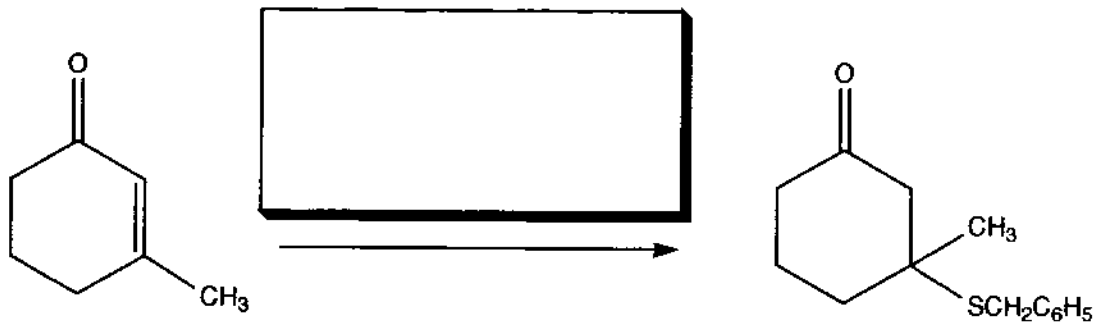
d) $CH_3CH_2O_2CCH_2CH_2CO_2CH_2CH_3$

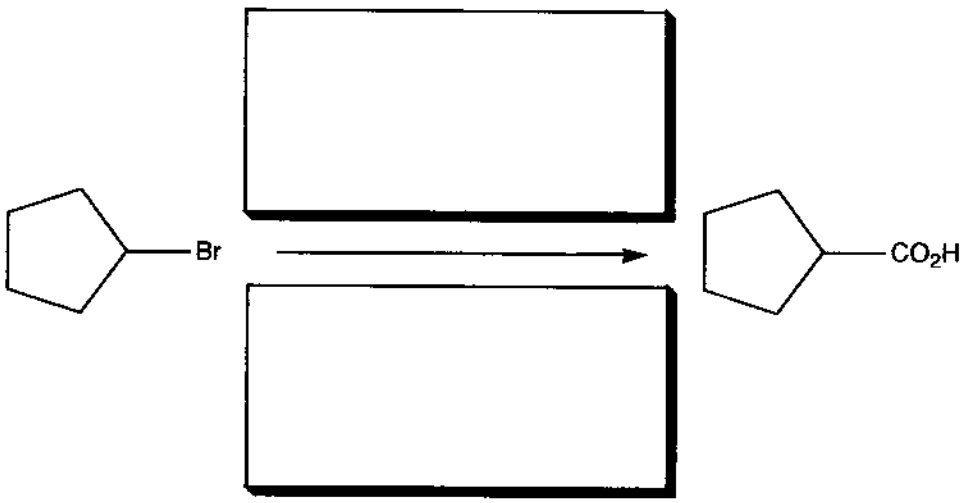
e) none of the above choices are correct

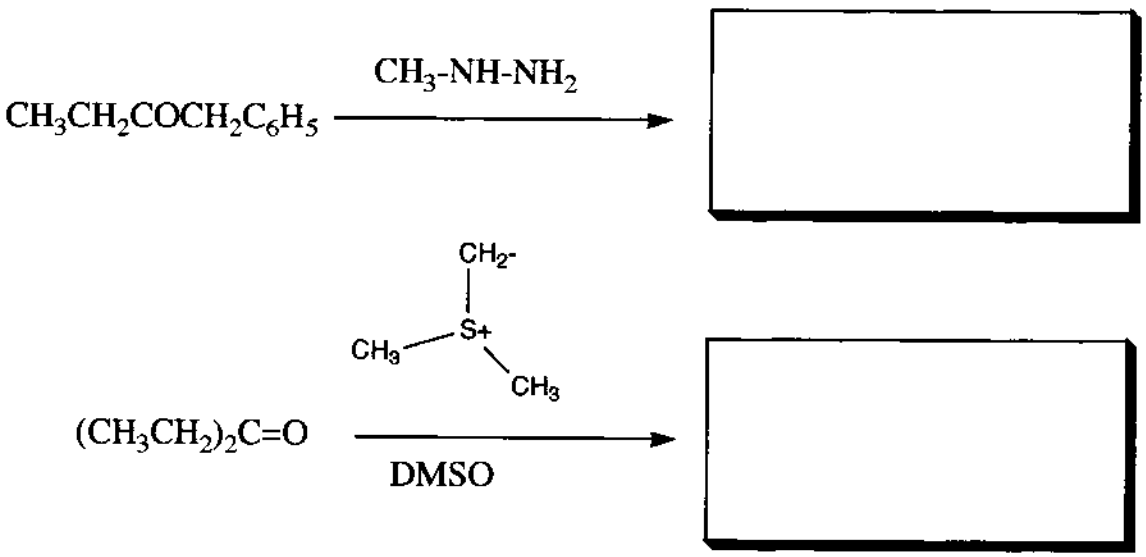
17. The reaction of $CH_3CH_2CH_2CN$ with DIBAL in hexane at -78°, followed by an aqueous workup will yield A, whereas reaction with CH_3MgBr followed by an aqueous acidic workup will yield B. A and B are: (in your choice, both must be correct)

	A	B
a)	butanoic acid	butanal
b)	isopropyl butanoate	methanol
c)	butanal	2-pentanone
d)	3-heptanone	propyl acetate
e)	butanol	2-butanol

14. continued...







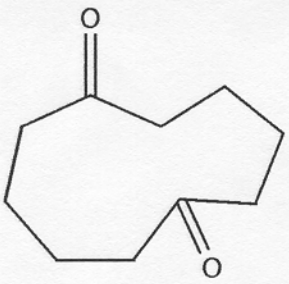
(18) 14. Write the missing products, reactants or reagents in the boxes:

OH^-

aldol

3

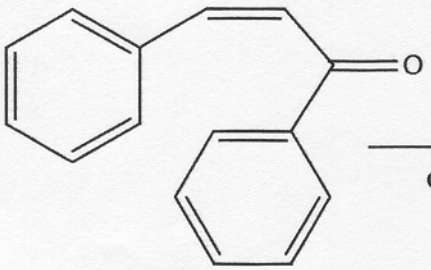
2-hydroxy-2-propylheptanal



OH^-

intramolecular aldol,
followed by elimination

a bicyclic enone, $C_{10}H_{14}O$



KCN

ethanol

IR 2250 cm^{-1}

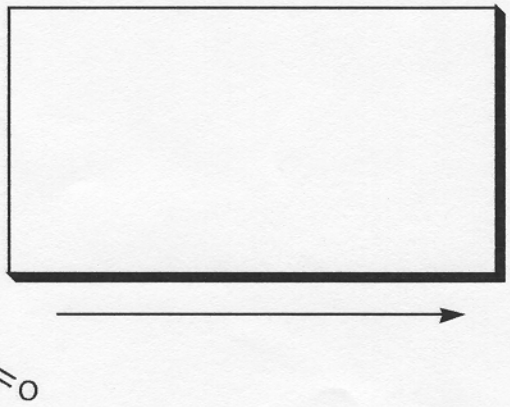
1690-1700 cm^{-1}

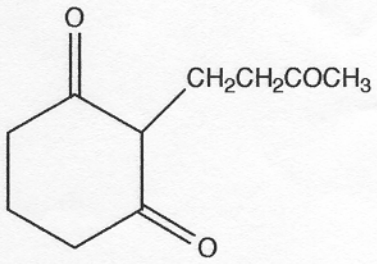
mass spec parent peak $M^+ = 235$

pmr 10H (m) near 7.0

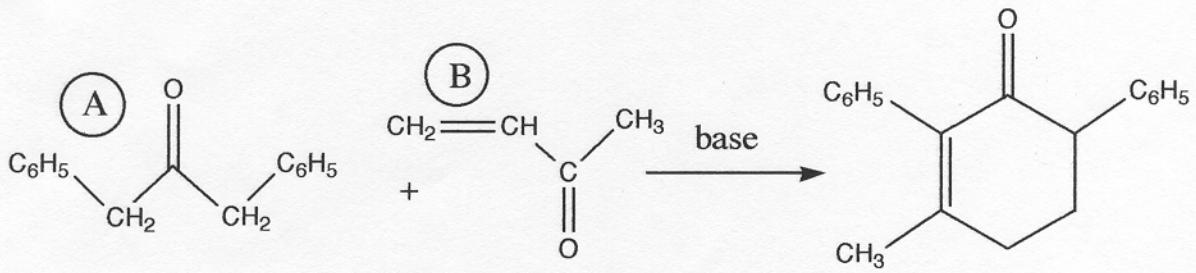
in addition to a doublet and triplet

upfield (3H) total





(4) 13. Write the complete mechanism for the following reactions:



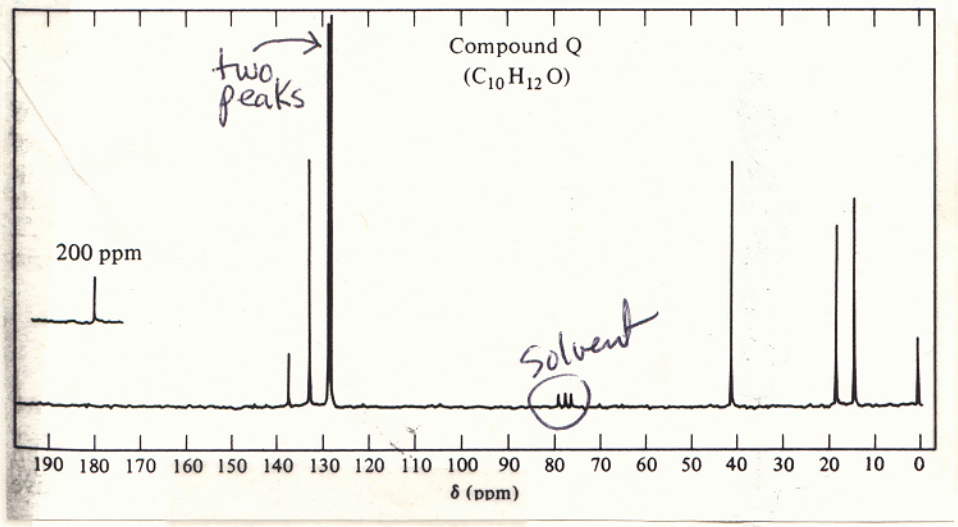
As a hint, here is a verbal description of the mechanism...

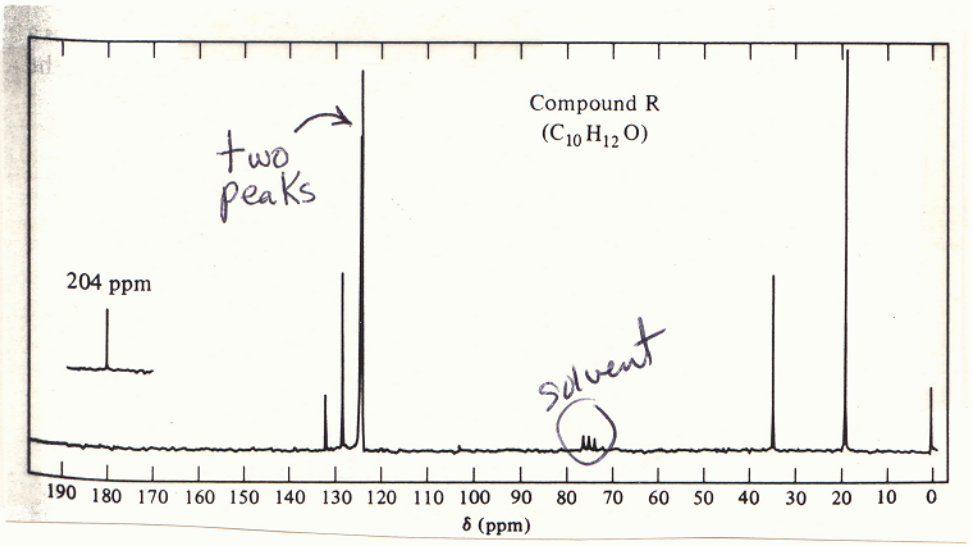
Begin with a conjugate addition (Michael addition) of dibenzyl ketone, A, on the methylvinyl ketone B. Tautomerize the enol formed back to the keto form. Cyclize the resulting diketone by an intramolecular aldol condensation. There are several intramolecular aldols which could occur, but only one leads to the product noted above. The last step is elimination of water.

(4) $CH_3CN \xrightarrow{H_3O^+,\ H_2O}$ acetic acid

Hint: Try protonating the nitrogen and then have water attack the nitrile carbon. After proton transfer the process repeats. Eventually the nitrogen is lost as ammonium ion.

(7) 12. Compounds Q and R are isomers having the molecular formula $C_{10}H_{12}O$. The mass spectrum of each compound contains an abundant peak at M/Z = 105. The cmr spectrum of each (totally decoupled) are shown below. Vigorous oxidation of R or Q yields benzoic acid. Identify both Q and R.



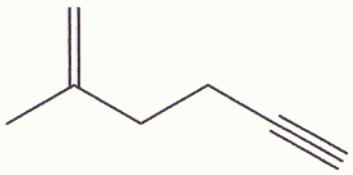


(3) 9. Aldehydes can easily be distinguished from ketones by looking at the off resonance decoupled cmr spectra of these carbonyl compounds. Explain!

(3) 10. A major mass spectral peak for aldehydes, in addition to a prominent parent peak, appears at M-1. What fragment might this be?

(3) 11. The IR spectra of simple aldehydes and ketones shows strong C=O absorption in what wave-number region? Conjugation (i.e., C=C-C=O) shifts this to a higher or lower energy?

(6) 7. Name the following compounds (IUPAC):



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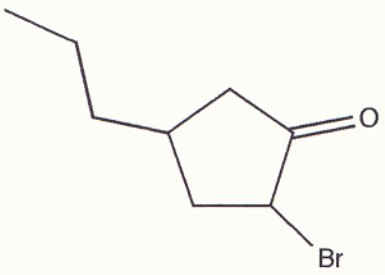

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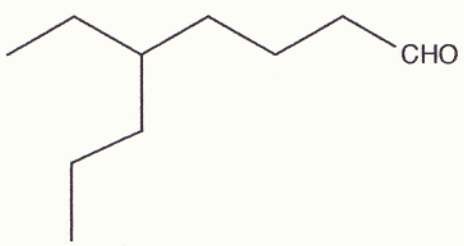

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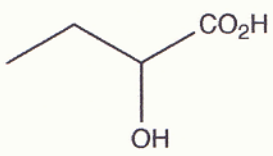
(6) 8. Name the following compounds (common nomenclature)



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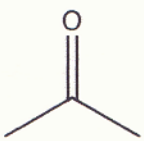

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CH_2O _____