

CHEM 20B3 Summer 2013

S. Knight & G. Bahun

Midterm Examination - July 18th, 6:00 - 8:00 p.m.

NAME _____

STUDENT NUMBER _____

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO.

THIS TEST CONSISTS OF 18 PAGES. You are responsible for ensuring that your copy of the test paper is complete. Bring any discrepancy to the attention of the invigilator **BEFORE** you begin writing the test. You are permitted to use molecular models and the standard McMaster standard calculator (Casio FX 991). **NO OTHER AIDS ARE ALLOWED!** Tables of spectral and other data are provided on pages 17 to 18.

THIS TEST IS IN TWO PARTS. PART I CONSISTS OF 20 MULTIPLE CHOICE QUESTIONS (WORTH 2 MARKS EACH) TO BE ANSWERED ON THE SCANTRON EXAMINATION SHEET. INSTRUCTIONS ARE PROVIDED ON PAGE 2.

PART II IS AND CONSISTS OF 5 QUESTIONS (TOTALLING 52 MARKS) . READ THE QUESTIONS CAREFULLY. WRITE YOUR SOLUTIONS NEATLY IN THE SPACES PROVIDED. NO OTHER FORMAT WILL BE ACCEPTED.

NOTE: IT IS EXTREMELY IMPORTANT TO MAKE SURE YOUR SCANTRON SHEET IS PROPERLY COMPLETED, OTHERWISE YOU WILL LOSE MARKS.

Remember to ENTER YOUR VERSION NUMBER, which can be found on the top right hand corner of this page, by filling in the BUBBLE in the “version” column provided. Finally, BUBBLE in your STUDENT number. Now CHECK all of your entries.

Q21	Q22	Q23	Q24	Q25	TOTAL	MC
12	11	10	9	10	52	40

STUDENT INSTRUCTIONS

Answer ALL the MC questions in Part I on optical scan sheets. You will not be penalized for incorrect answers. The MC questions are of equal value, and are worth a total of 40 marks. Failure to follow instructions below and on the optical scan sheets may result in loss of credit. Scan sheets will not be re-marked under any circumstances. You are responsible for ensuring all answers are in the correct place, and that you follow the correct procedure for filling out the scan sheet. **FILL IN THE BUBBLES DURING THE ALLOTTED EXAM TIME!**

NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED. YOUR EXAMINATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

The scanner, which reads the sheets, senses the bubble shaded areas by their non-reflection of light. **A heavy mark must be made, completely filling the circular bubble, with an HB pencil.** Marks made with a pen will **NOT** be sensed. Erasures must be thorough or the scanner will still sense a mark. Do **NOT** use correction fluid on the sheets. Do **NOT** put any unnecessary marks or writing on the sheet.

1. On **SIDE 1 (red side)** of the form, in the top box, print your student number, name, course name, and the date in the spaces provided, *in pen*. Then you **MUST** write your signature, in the space marked SIGNATURE.
2. In the second box, mark your **student number** and **test or exam version number (1, 2, 3 ...)** by filling in the corresponding bubbles underneath, *in pencil*.
3. Answers: mark only **ONE** choice from the alternatives (A,B,C,D,E) provided for each question. The question number is to the left of the bubbles. Make sure that the number of the question on the scan sheet is the same as the number on the test paper. Begin answering Question # 1 of Part I of this exam using the first set of bubbles, marked "1". Do Not use Side 2.

STUDENT NUMBER	NAME <small>(Surname) (Given Names)</small>	 McMaster University EXAMINATION ANSWER SHEET
SHEET # _____ OF _____	SIGNATURE <small>(in pen)</small>	
COURSE <small>(Name and Number - e.g. ENGL101 140)</small>		SECTION <small>(e.g. 01, 02, 03)</small>

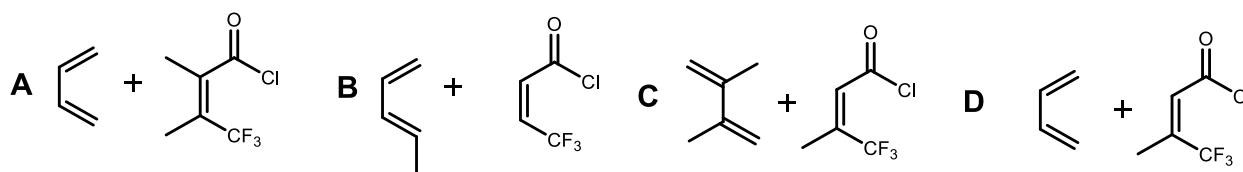
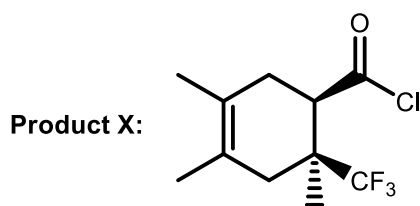
STUDENT NUMBER	VERSION	SECTION NO.	SEAT NUMBER			MARKING DIRECTIONS	EXAMPLES
			ROOM	ROW	SEAT		
00	00	00	00	00	00	• Use HB black lead pencil only. • Do not use ink or ballpoint pens. • Make heavy black marks that fill the circle completely. • Erase cleanly any answer you wish to change. • Make no stray marks on the answer sheet.	WRONG 1 (1) X (3) (4) (5) WRONG 2 (1) (2) (3) (4) (5) WRONG 3 (1) (2) (3) (4) (5) RIGHT 4 (1) (2) (3) (4) (5)
01	01	01	01	01	01		
02	02	02	02	02	02		
03	03	03	03	03	03		
04	04	04	04	04	04		
05	05	05	05	05	05		
06	06	06	06	06	06		
07	07	07	07	07	07		
08	08	08	08	08	08		
09	09	09	09	09	09		
10	10	10	10	10	10		
11	11	11	11	11	11		
12	12	12	12	12	12		
13	13	13	13	13	13		
14	14	14	14	14	14		
15	15	15	15	15	15		
16	16	16	16	16	16		
17	17	17	17	17	17		
18	18	18	18	18	18		
19	19	19	19	19	19		
20	20	20	20	20	20		
21	21	21	21	21	21		
22	22	22	22	22	22		
23	23	23	23	23	23		
24	24	24	24	24	24		
25	25	25	25	25	25		

Section 1: MULTIPLE CHOICE [Questions 1-20 are 2 marks each]

Question 1: Which of the following statements about the vinylic radical is TRUE?

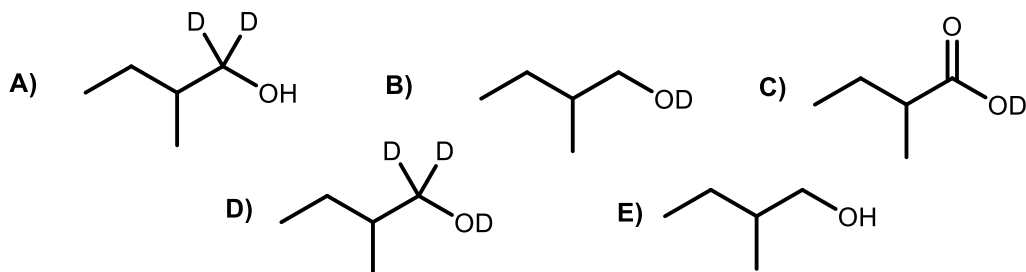
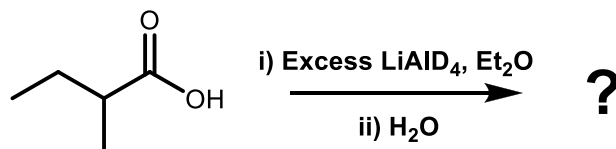
- a) It is less stable than an allylic radical, but more stable than a methyl radical
- b) It is stabilized through hyperconjugation
- c) It is not stabilized through hyperconjugation
- d) It will form preferentially over a radical at the allylic position
- e) None of the above statements are true

Question 2: Which combination of reagents will yield the product X?

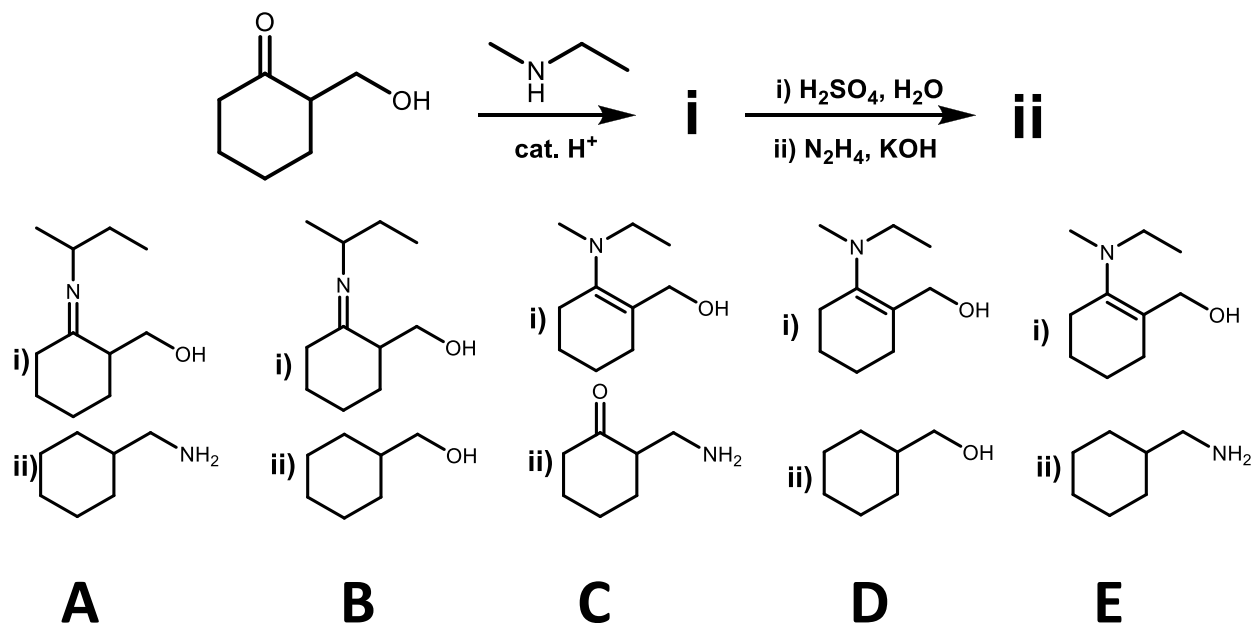


- f) none of the above

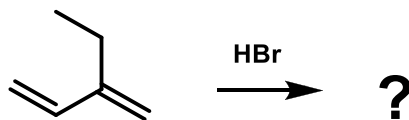
Question 3: What product would you expect from the following reaction?



Question 4: What pair of products (i and ii) will be formed from the following synthetic steps?

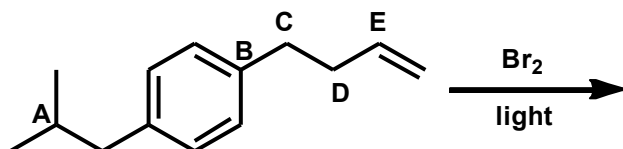


Question 5: How many unique products are formed in the following reaction, including all minor products?



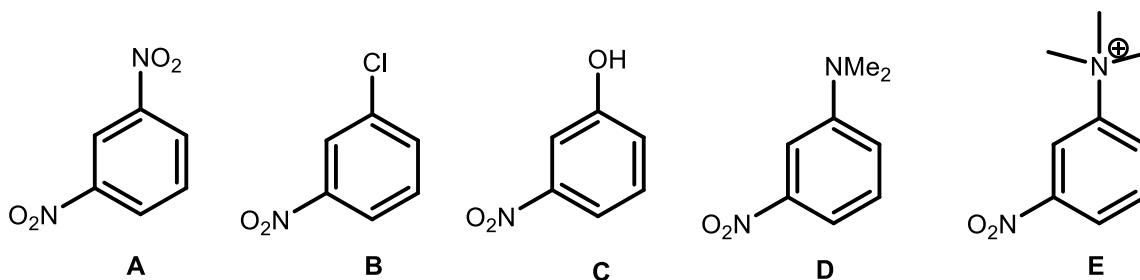
- a) 2
- b) 3
- c) 4
- d) 5
- e) 6

Question 6: In the following radical halogenation, which process would you expect to occur the fastest?

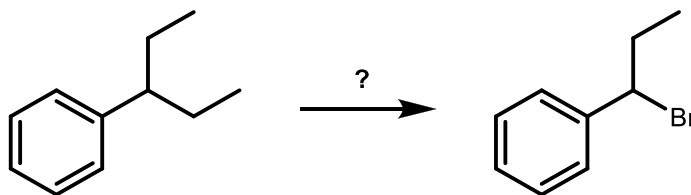


- a) hydrogen abstraction at position B
- b) hydrogen abstraction at position A
- c) hydrogen abstraction at position D
- d) hydrogen abstraction at position E
- e) hydrogen abstraction at position C

Question 7: Which compound would you expect to react the fastest with 2-bromopropane in the presence of iron(III) bromide catalyst?



Question 8: What synthetic steps (in **bold**) would you use to complete the following transformation?



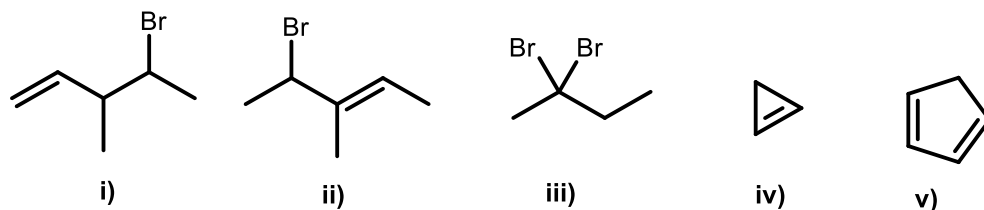
i) **1.** $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$ **2.** $\text{LiAlH}_4, \text{Et}_2\text{O}$ **3.** H_2O **4.** PBr_3

ii) **1.** $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$ **2.** $\text{LiAlH}_4, \text{Et}_2\text{O}$ **3.** H_2O **4.** $\text{PCC}, \text{CH}_2\text{Cl}_2$ **5.** $\text{EtMgBr}, \text{Et}_2\text{O}$ **6.** H_2O . **7.** PBr_3

iii) **1.** $\text{KMnO}_4, \text{NaOH}, \text{H}_2\text{O}$ **2.** $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ **3.** $\text{NaBH}_4, \text{Et}_2\text{O}$ **4.** $\text{PCC}, \text{CH}_2\text{Cl}_2$ **5.** $\text{EtMgBr}, \text{Et}_2\text{O}$ **6.** H_2O . **7.** PBr_3

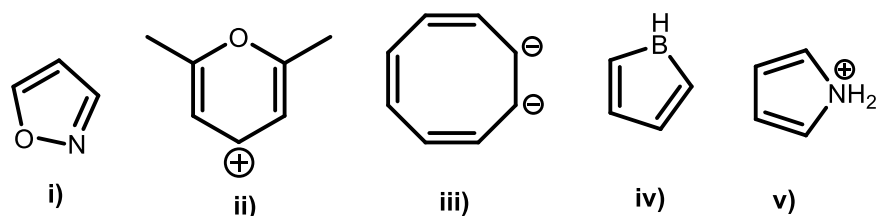
- a) i and ii
- b) ii
- c) iii
- d) ii and iii
- e) i and iii

Question 9: Which of the following would you react with potassium tert-butoxide to create a new conjugated system?



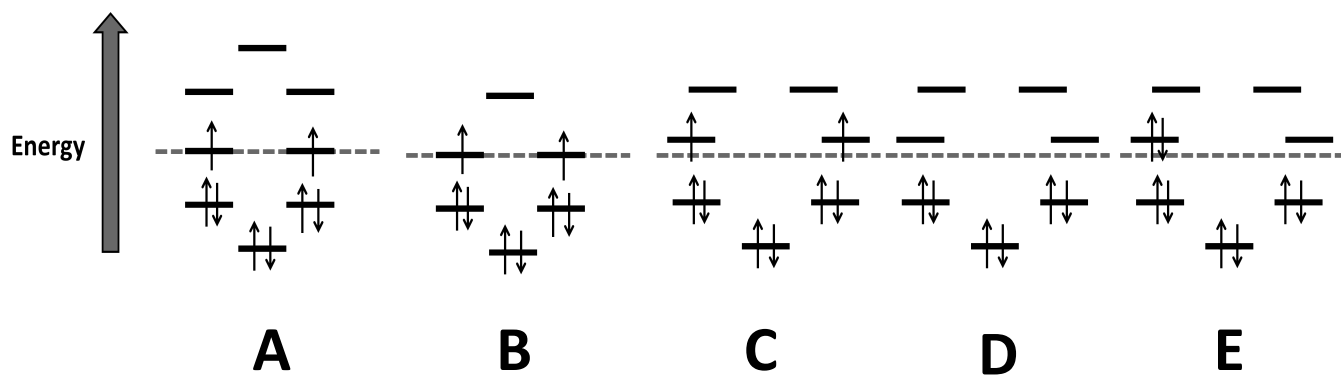
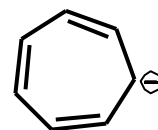
- a) i, iii
- b) i, ii, iv
- c) iii, iv, v
- d) ii, iii, iv, v
- e) ii, v

Question 10: Which of the following rings are aromatic?

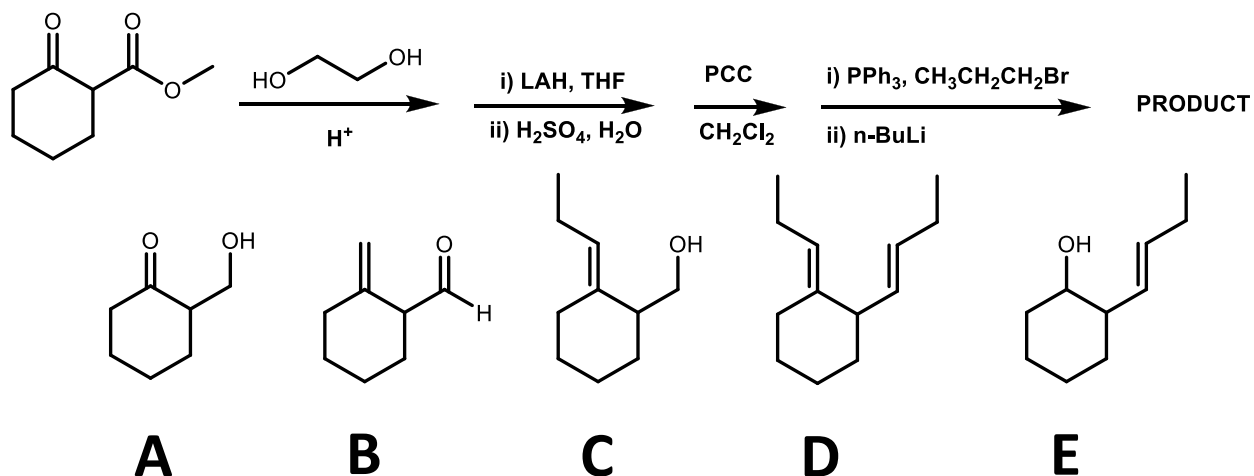


- a) i, ii
- b) i, ii, iii
- c) ii, iv
- d) ii, iv, v
- e) ii, iii, iv

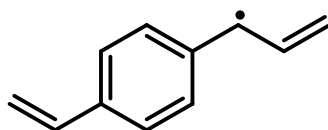
Question 11: Which Frost-Circle Diagram represents the cycloheptatrienyl anion ?



Question 12: What is the product of the following reaction sequence?



Question 13: How many resonance structures in total does the following contributor have (NOT including the structure shown OR the rearrangement of electrons in a benzene ring)?



- 4
- 5
- 6
- 7
- 8

Question 14: Select the FALSE statement(s) about the benzylic radical below:

- The benzylic radical is more stable than the allylic radical due to hyperconjugation.
- The benzylic radical formed from toluene has 4 significant resonance contributors.
- When a benzylic radical is formed, radical halogenation will likely occur directly on the benzene ring in addition to at the benzylic position.
- The benzylic radical forms an empty p-orbital at the benzylic carbon.

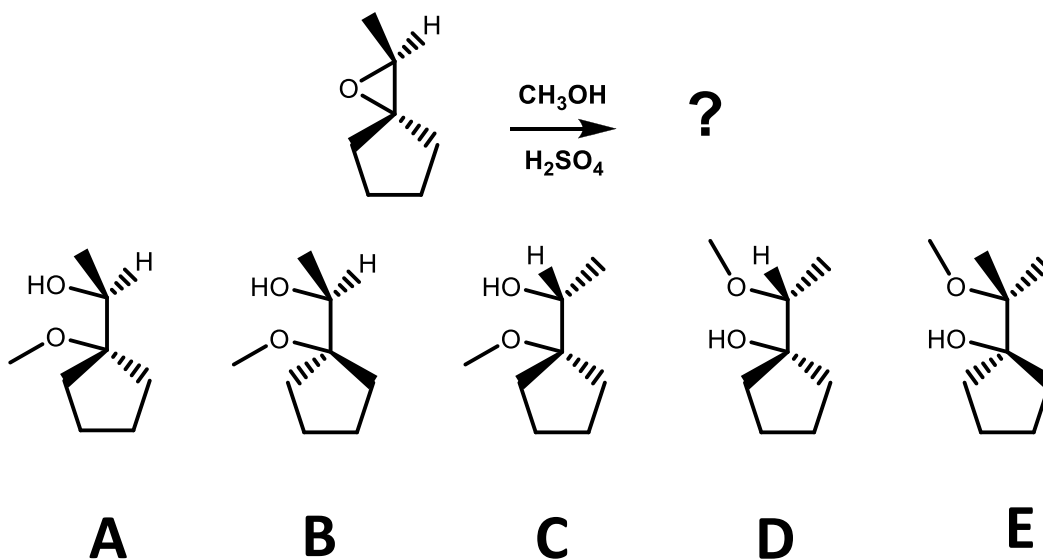
- i
- ii, iii, iv
- iii
- i, iii, iv
- i, ii, iii, iv

Question 15: Select the FALSE statement(s) about ethers and alcohols below:

- Dimethyl ether has a lower boiling point than 1-propanol.
- Both dimethyl ether and 1-propanol experience intermolecular hydrogen bonding.
- Dimethyl ether is more likely to be a vapour at 60° C than 1-propanol.
- Dimethyl ether is more miscible with water than 1-propanol.

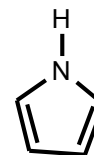
- i
- i, iii
- ii, iv
- ii
- iv

Question 16: Which of the following represents the product formed from the following reaction?



Question 17: Which of the following statements about pyrrole is FALSE?

- The nitrogen atom is sp² hybridized.
- The single lone-pair of electrons is delocalized.
- The ring is aromatic.
- Pyrrole is not basic.
- The single lone-pair of electrons occupies an sp² hybrid orbital.



Question 18: Which of the following conditions must be met for a ring to potentially be aromatic?

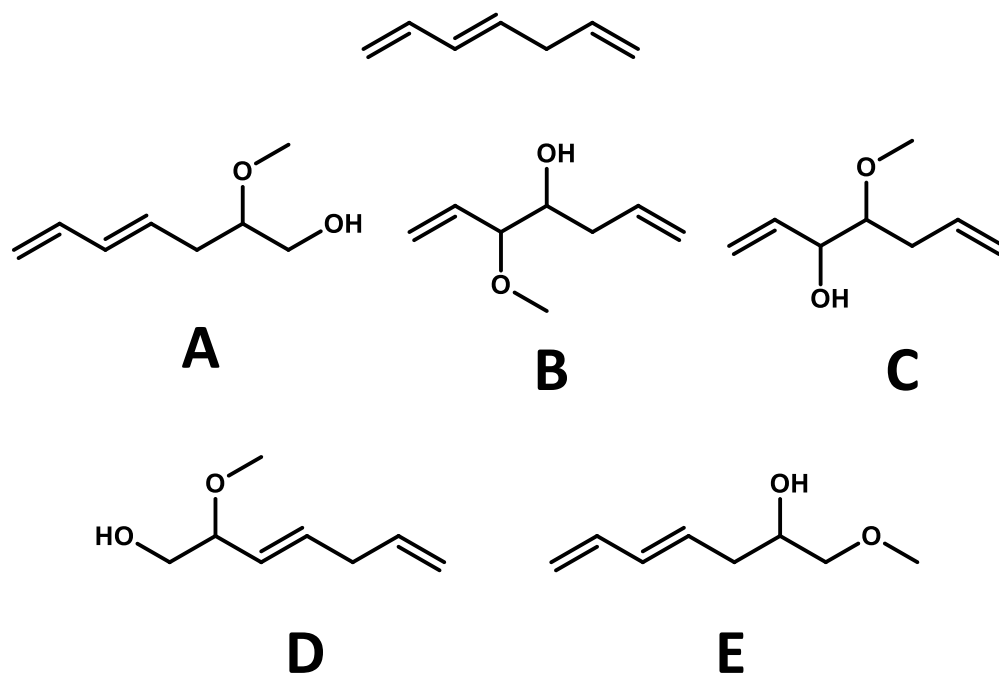
- It must have a total of $(4n)\pi$ or p-orbital electrons.
- All atoms in the ring must be sp^2 hybridized.
- The ring must not contain heteroatoms.
- Atoms attached to the ring must be sp^2 hybridized.
- It must have a total of $(4n+2)\pi$ or p-orbital electrons.

- ii, iv, v
- ii, v
- i, ii
- ii, iii, v
- v

Question 19: Which of the following reagents/sets of reagents would convert methyl benzoate to 3-phenylpentan-3-ol?

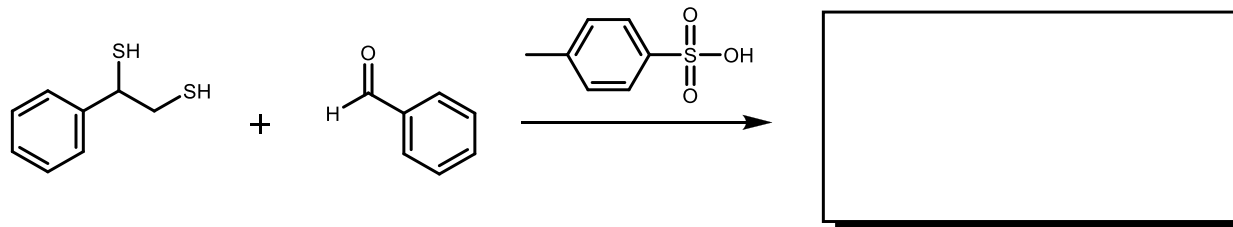
- i.** 2 equiv. EtMgBr **ii.** H₂O
- i.** 2 equiv. NaOEt/EtOH **ii.** H₂O
- i.** NaH **ii.** 2 Equiv. CH₃CH₂I
- i.** NaOEt **ii.** 2 Equiv. CH₃CH₂I
- none of the above.

Question 20: Which of the following represents the product when the triene shown is combined with meta-chloroperoxybenzoic acid, then methanol in the presence of a catalytic amount of acid?



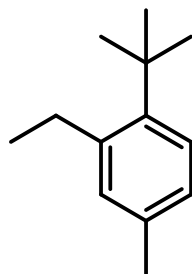
Section 2: WRITTEN ANSWER - Record your answer in the space provided

Question 21: Give the product of the following reaction in the box. SHOW A COMPLETE MECHANISM FOR THE REACTION in the space provided [12 marks].

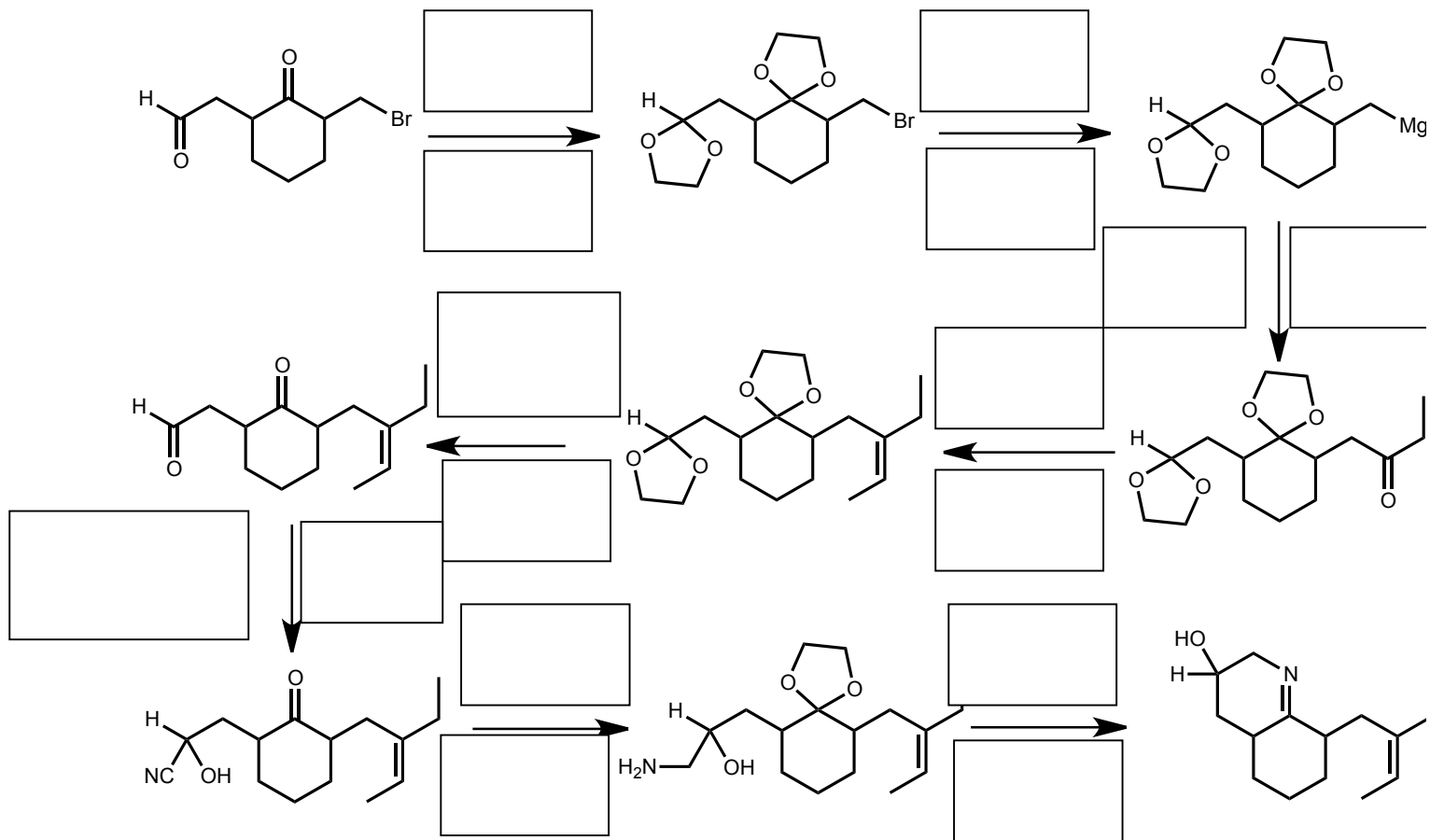


MECHANISM:

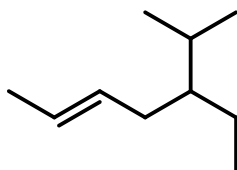
Question 22: Starting from benzene, provide a total synthesis of the following molecule. You do not need to show the mechanism, only the reagents and intermediate compounds produced [11 marks].



Question 23: Provide reagents as necessary to complete the overall reaction mechanism. You may need to show multiple steps over a single arrow, so be sure to CLEARLY DELINEATE these steps for full marks. Be sure to give numbers of equivalents, conditions (temperature) and solvents where appropriate [10 marks].



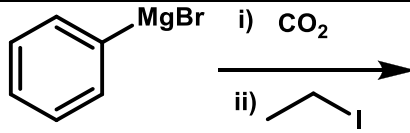
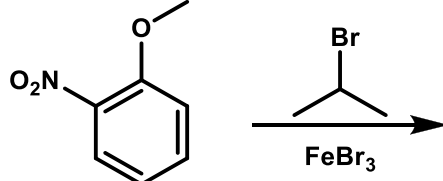
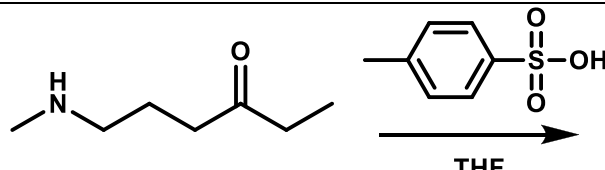
Question 24: Provide a retrosynthetic breakdown of the following molecule, starting from 3-methyl-2-butanol and any reagent containing 2 carbons or fewer [9 marks]:



SPACE FOR THIS PROBLEM IS PROVIDED ON THE FOLLOWING PAGE!

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Question 25: Choose 10 of the following 14 reactions and show the product formed in the space provided. If no reaction occurs, write no reaction. THE FIRST 10 ANSWERS WILL BE MARKED. If you do not wish to provide an answer, LEAVE THE SPACE BLANK or cross out anything in the space [10 marks].

 <p>Phenylmagnesium bromide reacts with CO_2 followed by ethyl iodide.</p>	
 <p>3-nitroanisole reacts with isobutyl bromide in the presence of FeBr_3.</p>	
 <p>N-methyl-4-oxopentan-2-amine reacts with p-toluenesulfonic acid in THF.</p>	

<p>Reaction of 1-phenylethane-1,2-diol with formaldehyde (HCHO) in the presence of p-toluenesulfonic acid (TsOH) in THF.</p>	
<p>Reaction of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) with sodium hydride ($\text{NaH}$) followed by ethyl iodide ($\text{CH}_3\text{CH}_2\text{I}$).</p>	
<p>Reaction of 2,2-dimethyloxirane (propylene oxide) with methanol (CH_3OH) in the presence of sulfuric acid (H_2SO_4).</p>	
<p>Reaction of methyl 3-oxopropanoate ($\text{HCOCH}_2\text{CO}_2\text{CH}_3$) with sodium borohydride (NaBH_4) in THF.</p>	
<p>Reaction of methyl 3-oxopropanoate ($\text{HCOCH}_2\text{CO}_2\text{CH}_3$) with lithium aluminum hydride (LAH) in THF.</p>	
<p>Reaction of 1-(2,4,6-trimethylphenyl)cyclopentene with sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) and sulfuric acid ($\text{H}_2\text{SO}_4$).</p>	
<p>Reaction of 4-hydroxy-2-methylpentanal with pyridinium chlorochromate (PCC) in dichloromethane (CH_2Cl_2).</p>	
<p>Reaction of 4-hydroxy-2-methylpentanal with a Wittig reagent ($\text{Ph}_3\text{P}=\text{C}(\text{Me})_2$) in THF.</p>	
<p>Reaction of 3-hydroxybutanal with methylmagnesium bromide (CH_3MgBr) in diethyl ether (Et_2O).</p>	
<p>Reaction of 4-chloro-1-(trimethylsilyloxy)butan-1-one with tetrabutylammonium fluoride (TBAF).</p>	
<p>Reaction of benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$) with water ($\text{H}_2\text{O}$).</p>	

End of Midterm

At least I didn't ask you to synthesize: Aspirin, Tylenol, Tetrahydrocannabinol, Lysergic Acid Diamine, Methamphetamine, or Oxycodone. All of these are organic. You have been warned.

The following space is for ROUGH WORK ONLY. THEY WILL NOT BE GRADED!

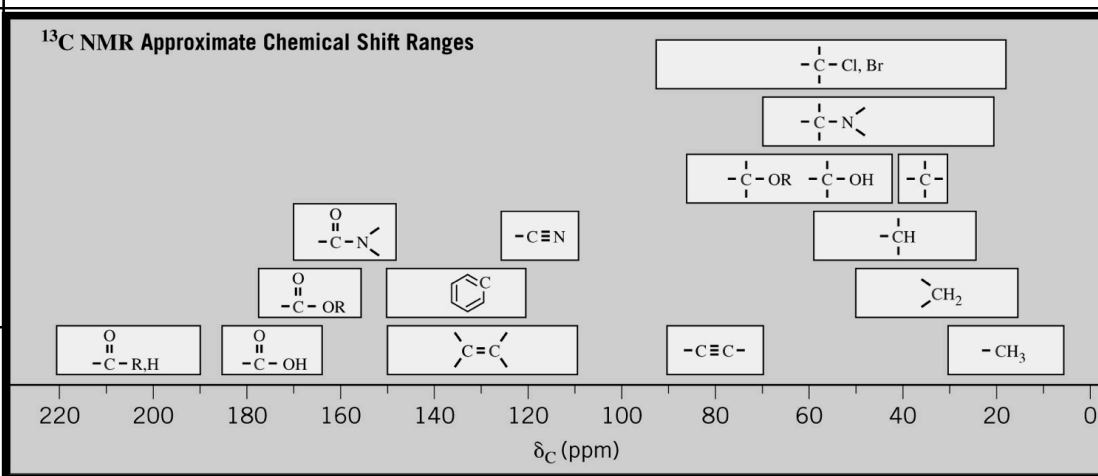
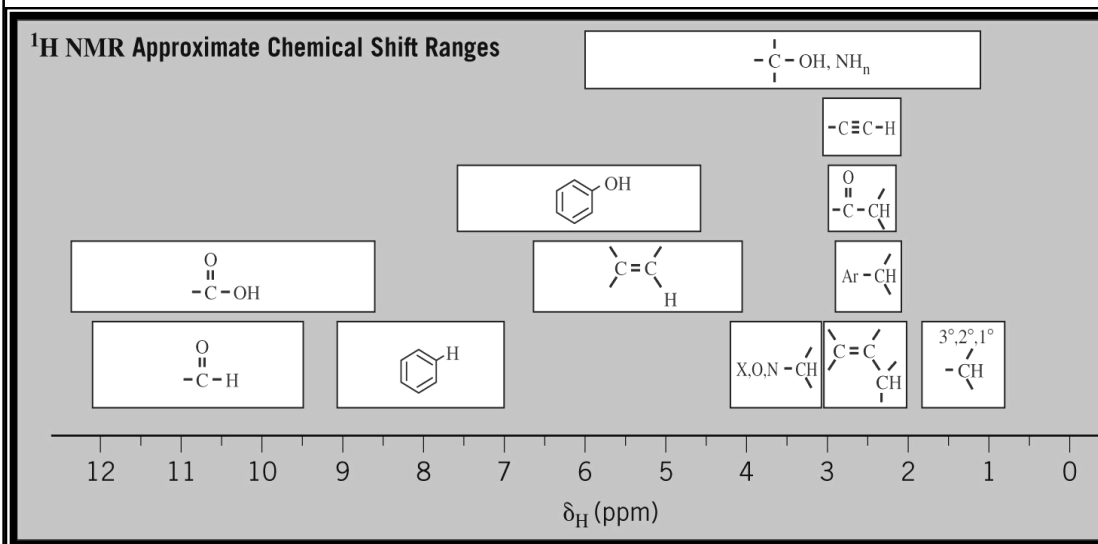
The following space is for ROUGH WORK ONLY. THEY WILL NOT BE GRADED!

PERIODIC TABLE OF THE ELEMENTS

1 H 1.008	2 He 4.002	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18	11 Na 22.99	12 Mg 24.30	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.38	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 127.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.0	89 Ac 227.0	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 145	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	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

Acid	pK_a
HI	-9
HBr	-8
HCl	-7
H ₂ SO ₄	-5.2
H ₃ O ⁺	-1.74
H ₃ PO ₄	2.1
CH ₃ CO ₂ H	4.76
H ₂ CO ₃	6.36
NH ₄ ⁺	9.24
HCO ₃ ⁻	10.33
H ₂ O	15.7
CH ₃ CH ₂ OH	15.9
CH ₃ C=OMe	20
HC≡CH	25
H ₂	35
NH ₃	38
CH ₂ =CH ₂	44
CH ₃ CH ₃	51



IR CORRELATION CHART:

Group	Frequency Range (cm ⁻¹)	Intensity ^a
A. Alkyl		
C—H (stretching)	2853–2962	(m–s)
Isopropyl, —CH(CH ₃) ₂	1380–1385	(s)
	and 1365–1370	(s)
<i>tert</i> -Butyl, —C(CH ₃) ₃	1385–1395	(m)
	and ~ 1365	(s)
B. Alkenyl		
C—H (stretching)	3010–3095	(m)
C=C (stretching)	1620–1680	(v)
R—CH=CH ₂	985–1000	(s)
R ₂ C=CH ₂	and 905–920	(s)
(out-of-plane C—H bendings)		
<i>cis</i> -RCH=CHR	675–730	(s)
<i>trans</i> -RCH=CHR	960–975	(s)
C. Alkynyl		
≡C—H (stretching)	~ 3300	(s)
C≡C (stretching)	2100–2260	(v)
D. Aromatic		
Ar—H (stretching)	~ 3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)		
Monosubstituted	690–710	(very s)
<i>o</i> -Disubstituted	and 730–770	(very s)
<i>m</i> -Disubstituted	735–770	(s)
	680–725	(s)
	and 750–810	(very s)
<i>p</i> -Disubstituted	800–860	(very s)
E. Alcohols, Phenols, and Carboxylic Acids		
O—H (stretching)		
Alcohols, phenols (dilute solutions)	3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)	3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)	2500–3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids		
C=O (stretching)	1630–1780	(s)
Aldehydes	1690–1740	(s)
Ketones	1680–1750	(s)
Esters	1735–1750	(s)
Carboxylic acids	1710–1780	(s)
Amides	1630–1690	(s)
G. Amines		
N—H	3300–3500	(m)
H. Nitriles		
C≡N	2220–2260	(m)

^aAbbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

END