

UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 24th, 2010

Time: 3 Hours

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON THE **COMPUTER ANSWER SHEET** AND THE **BOOKLET** FOR THE WRITTEN ANSWER QUESTIONS.

READ THE INSTRUCTIONS CAREFULLY

The examination consists of Parts 1 - 10, each of which should be attempted. Note that some Parts provide you with a choice of questions, e.g. answer 5 out of 6. These will be graded in order the answers appear until the required number have been completed, **regardless** of whether they are right or wrong.

Parts 1 - 6 will be computer graded, and Parts 7 - 10 are to be answered in the examination booklet. Parts 1 - 6 consist of a series of multiple choice questions numbered 1 - 50 which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and **not ink**. In some cases it is required that you indicate **multiple** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out **both** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased **cleanly**.

A periodic table with atomic numbers and atomic weights and tables of spectroscopic data are provided at the end of the examination paper. **No other resources are allowed.**

Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**.

Absolutely no other electronic devices are allowed.

12% **PART 1: RELATIVE PROPERTIES**

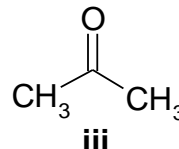
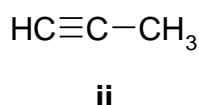
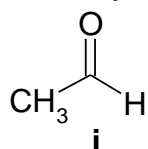
ANSWER ANY EIGHT (8) OF THE TEN (10) QUESTIONS 1-10.

Arrange the items in questions 1-10 in **DECREASING ORDER** (*i.e.* greatest, most etc. first) with respect to the indicated property. Use the following code to indicate your answers:

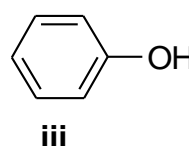
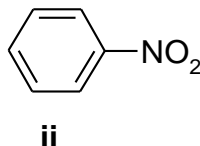
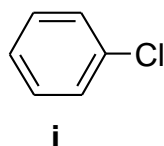
A **i > ii > iii**
B **i > iii > ii**
C **ii > i > iii**

D **ii > iii > i**
E **iii > i > ii**
AB **iii > ii > i**

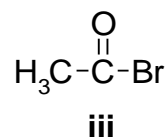
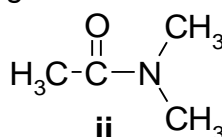
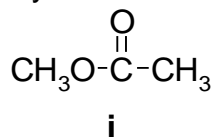
1. The relative acidity of the most acidic hydrogen in each of the following:



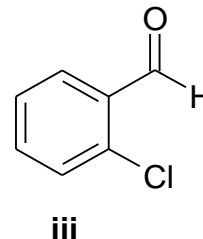
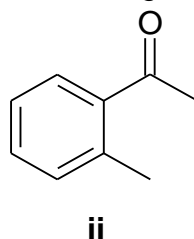
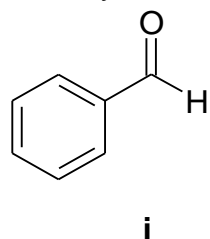
2. The relative rate of reaction of HNO₃/H₂SO₄ with each of the following:



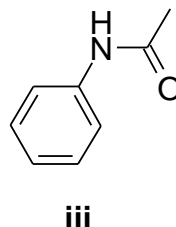
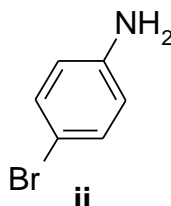
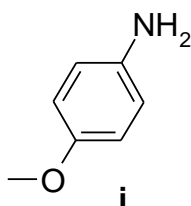
3. The relative reactivity towards benzyl magnesium bromide of each of the following:



4. The relative reactivity of each of the following towards reaction with LiAlH₄:



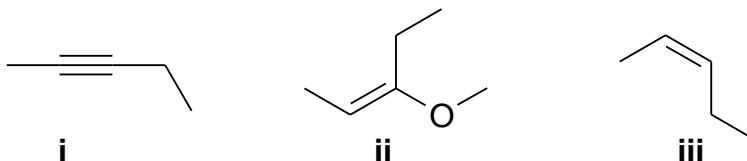
5. The relative basicity of each of the following:



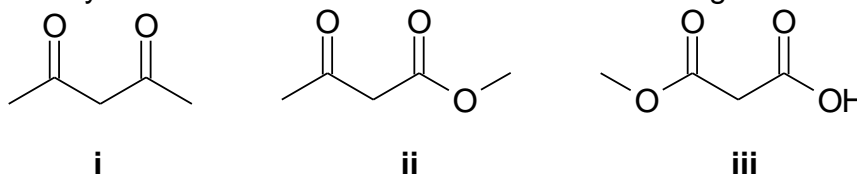
Use the following code to indicate your answers:

- | | | | |
|----------|---------------------------|-----------|---------------------------|
| A | i > ii > iii | D | ii > iii > i |
| B | i > iii > ii | E | iii > i > ii |
| C | ii > i > iii | AB | iii > ii > i |

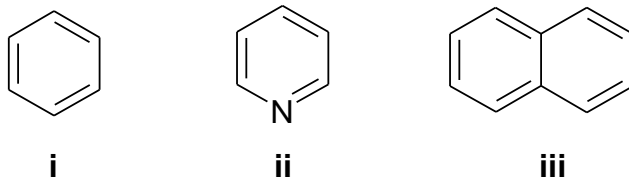
6. The relative reactivity of each of the following towards HBr / dark :



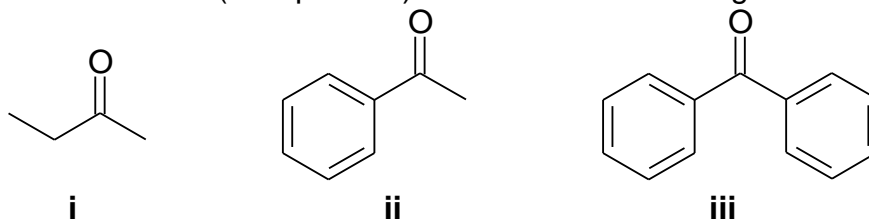
7. The relative acidity of the most acidic H in each of the following :



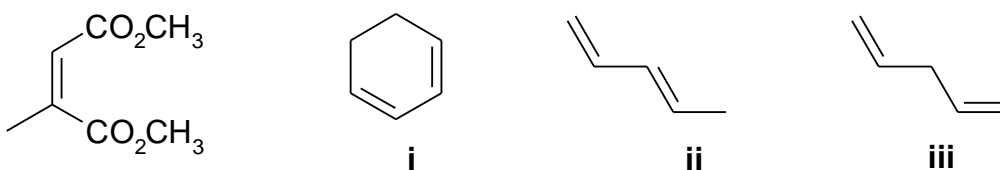
8. The resonance energy of each of the following:



9. The number of enolizable (or α -protons) in each of the following:



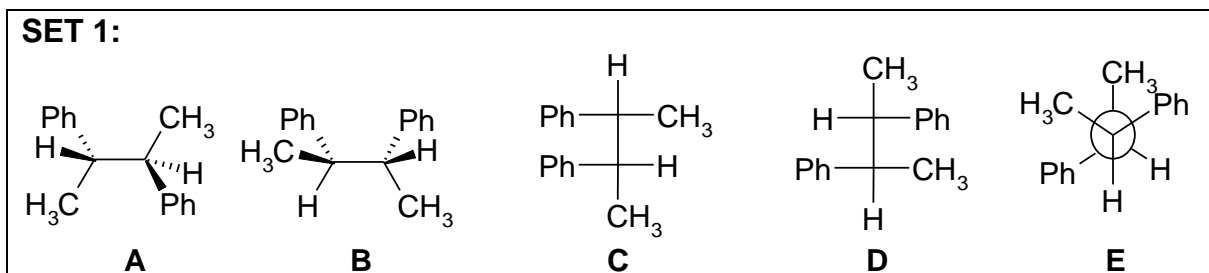
10. The number isomeric products from the reaction of each the following with *cis* dimethyl 2-methylbutendioate (shown below):



10 % **PART 2: STRUCTURE AND PROPERTIES**

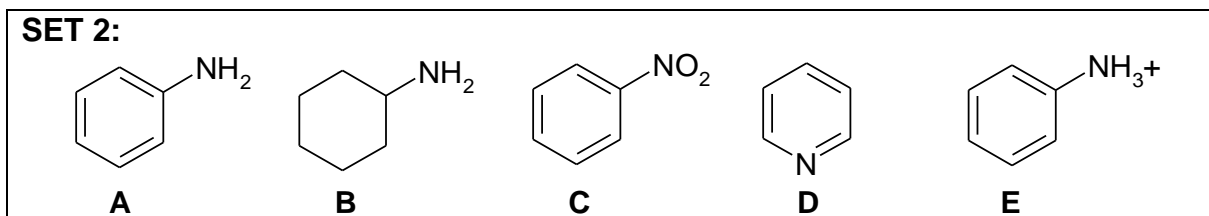
ANSWER ANY TEN (10) OF THE TWELVE (12) QUESTIONS 11-22.

In some cases more than one answer may be correct and ALL compounds that apply MUST be selected for full credit.



Answer questions 11-14 by selecting the compounds from SET 1 above.

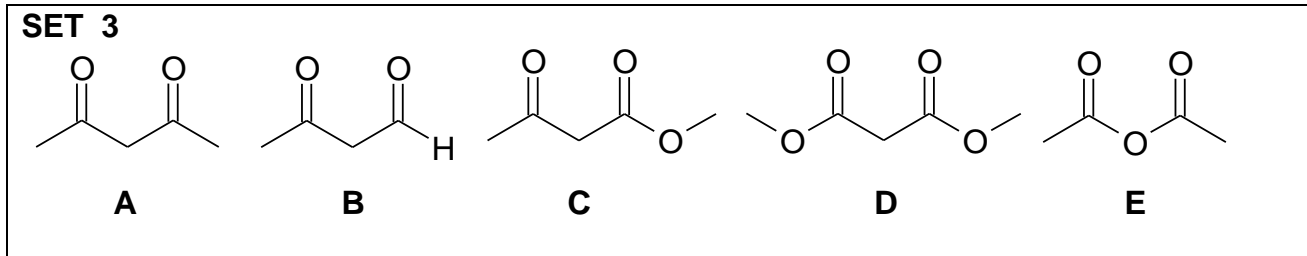
11. Select **ALL** the compounds that do not rotate plane polarized light
12. Select **ANY TWO** compounds that are a pair of enantiomers
13. Select **ALL** the structures that are the result of a metal catalyzed hydrogenation of a *trans* alkene.
14. Select **ANY TWO** structures that rotate plane polarized light in the same direction.



Answer questions 15-17 by selecting the compounds from SET 2 above.

15. Select the most basic structure.
16. Which structure(s) has (have) a N atom with a non-zero formal charge ?
17. Which structures form diazonium salts when reacted with NaNO_2 in HCl ?

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Answer questions 18-21 by selecting the compounds from SET 3 above.

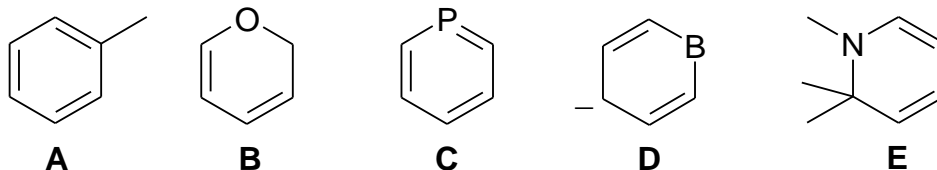
18. Which compound is the most acidic ?
19. Which compound is the least acidic ?
20. Which compounds do not react with NaBH_4 ?
21. Which compounds when reacted with H_3O^+ / heat, produce CO_2 gas ?

9% **PART 3: AROMATICITY AND RESONANCE**

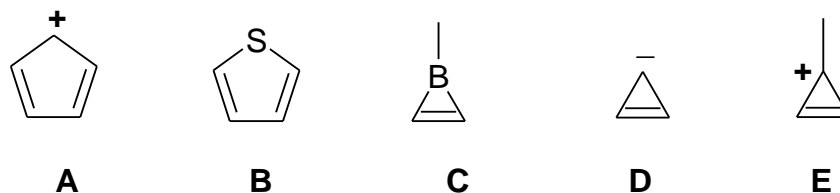
ANSWER ANY SIX (6) OF THE SEVEN (7) QUESTIONS 23 - 29.

For each of the questions 23-29 select **ALL the compounds** from the lists provided that matches each of the specific descriptions:

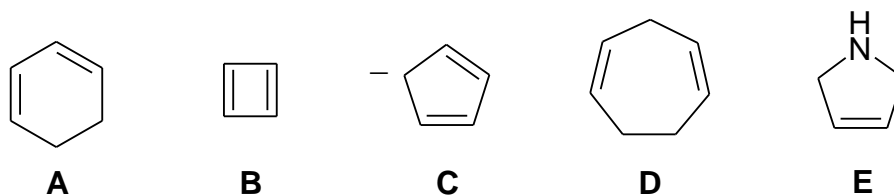
23. Molecules that are aromatic as drawn.



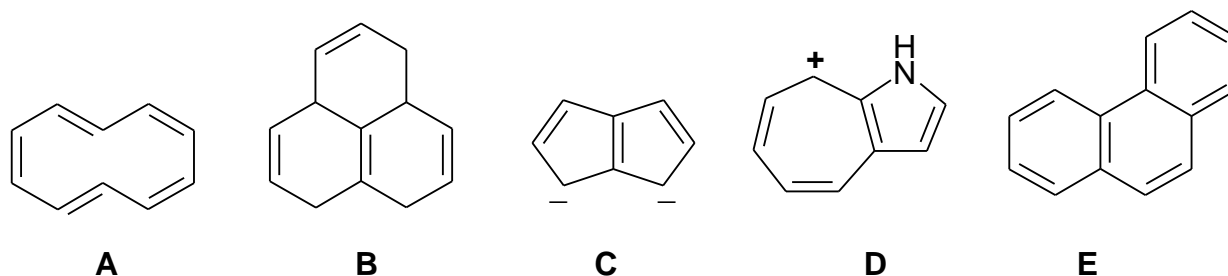
24. Molecules that are antiaromatic as drawn.



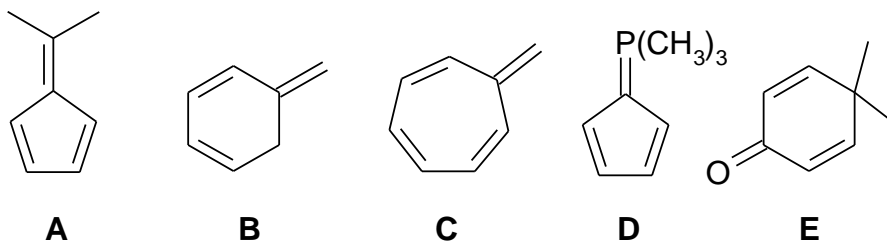
25. Molecules that are conjugated but non-aromatic as drawn.



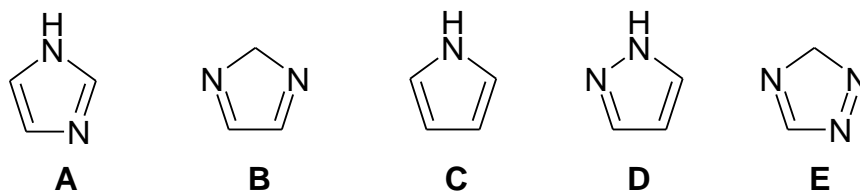
26. Molecules that are aromatic hydrocarbons where $n=2$ in the Hückel rule.



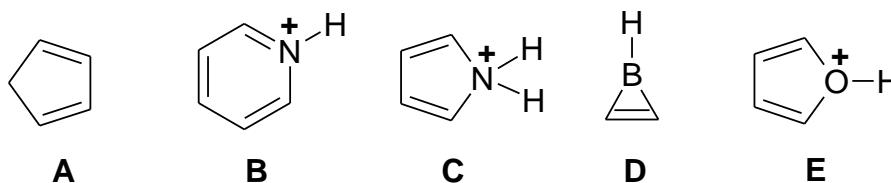
27. Molecules that are non-aromatic as drawn, but have an aromatic resonance contributor.



28. Molecules that are aromatic as drawn and have an aromatic conjugate acid.



29. Molecules that are non-aromatic as drawn and have an aromatic conjugate base.

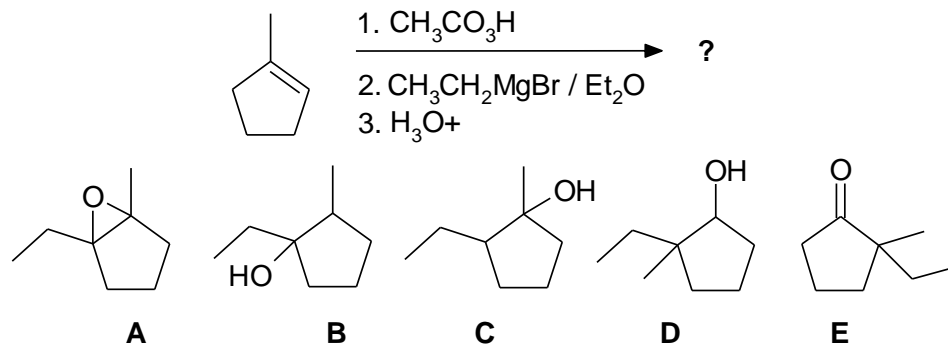


16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

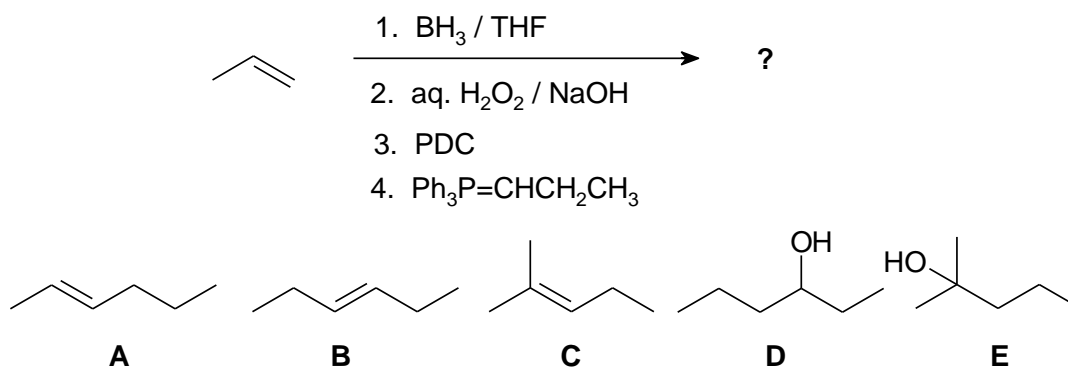
ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 30-38.

For each of the questions 30 - 38 identify the product(s) obtained or starting material(s) required in order to complete each of the reaction sequences shown by selecting from the list provided. In some cases more than one answer may be correct and ALL compounds that apply MUST be selected for full credit.

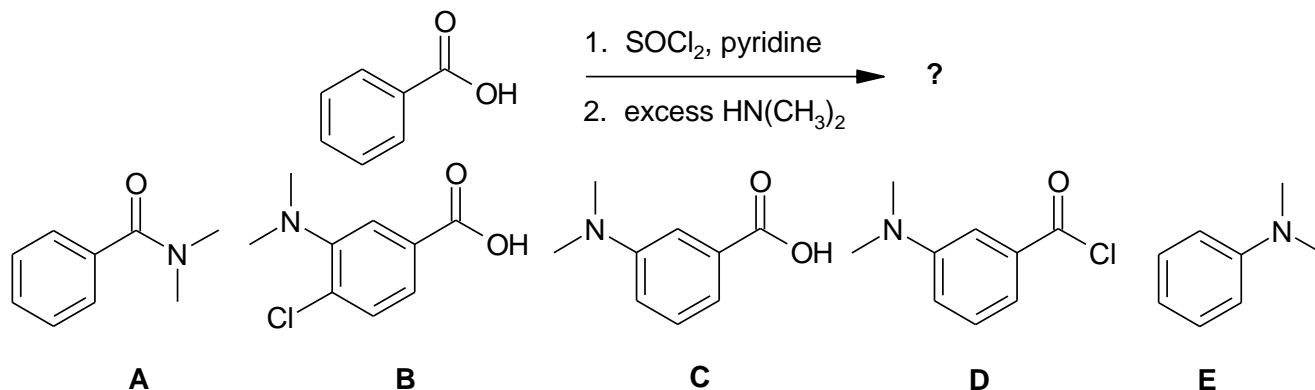
30.



31.

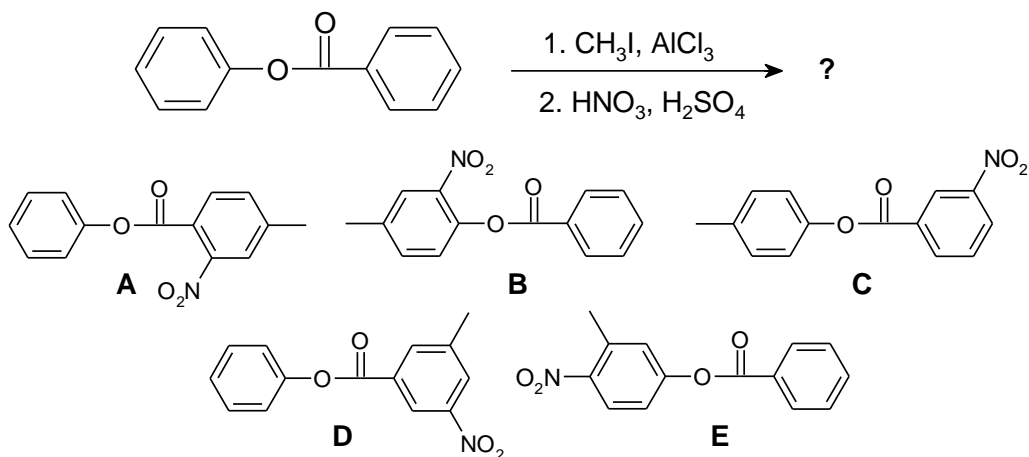


32.

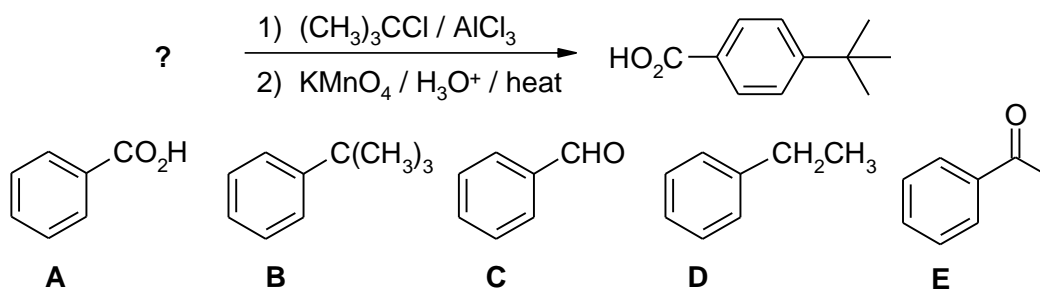


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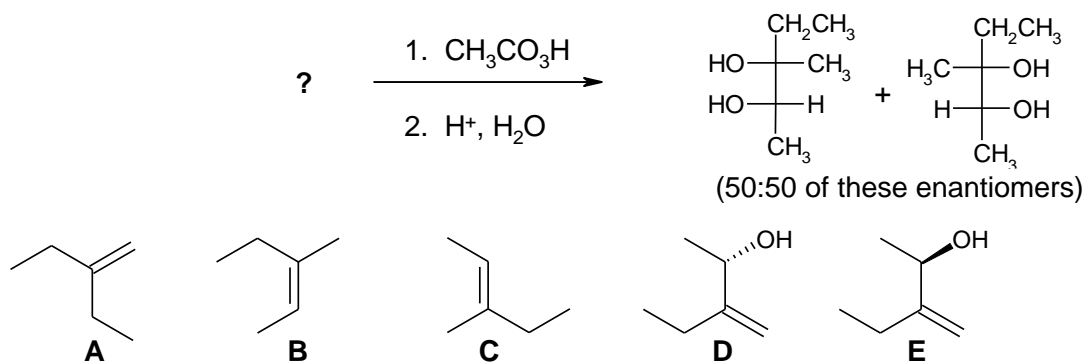
33.



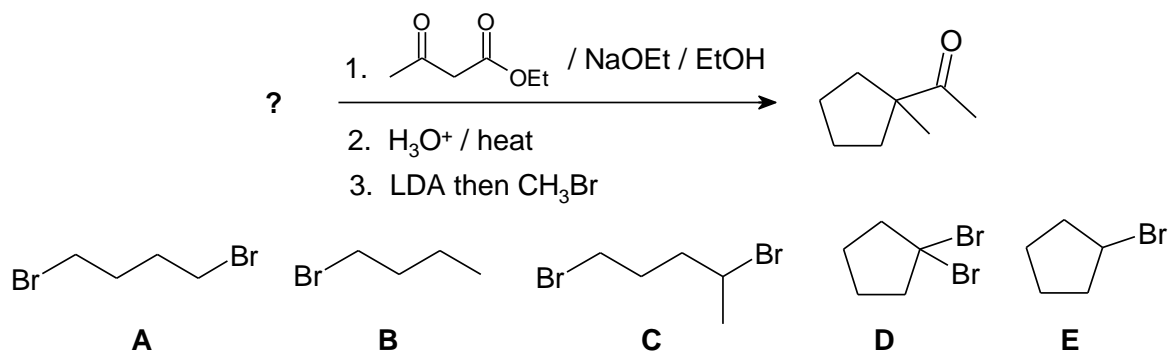
34.



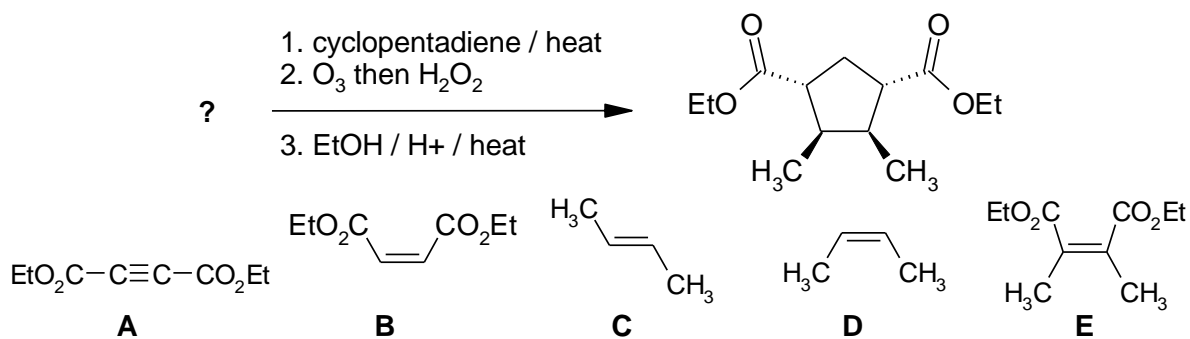
35.



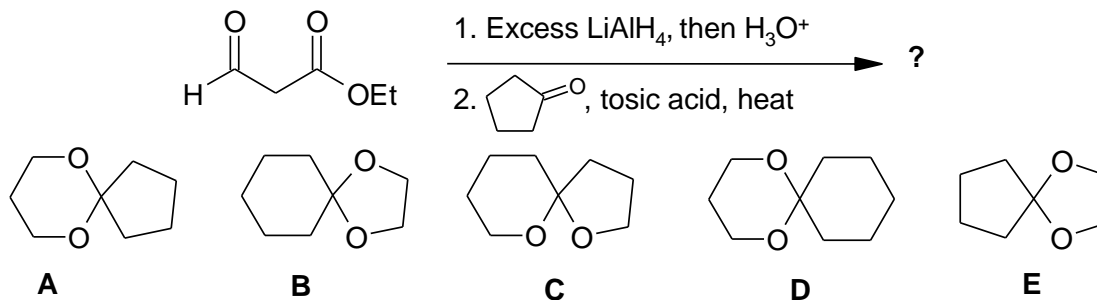
36.



37.



38.

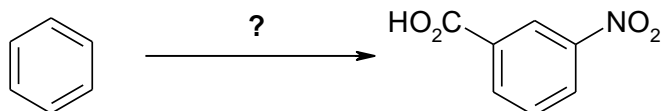


7.5% PART 5: REAGENTS FOR SYNTHESIS

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 39-44

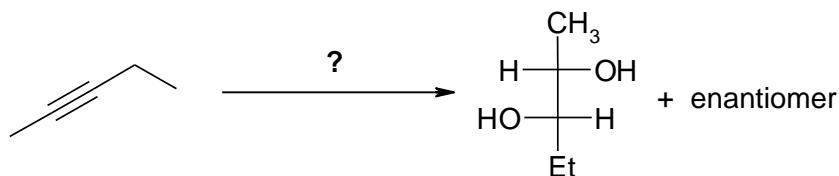
For each of the questions 39-44 identify the reagent sequence required in order to complete each of the reaction sequences shown by selecting from the list provided.

39.



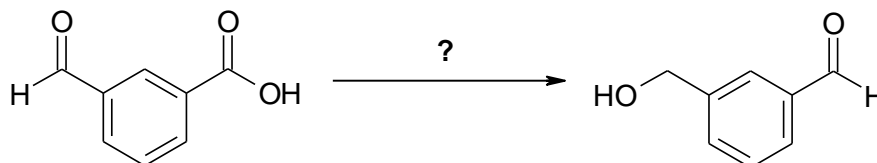
- A. i. Br₂ / FeBr₃ ii. HNO₃ / H₂SO₄ iii. Mg iv. CO₂, H⁺ workup
 B. i. Ethanoyl chloride, AlCl₃ ii. KMnO₄, H₃O⁺, heat iii. HNO₃ / H₂SO₄
 C. i. HNO₃ / H₂SO₄ ii. Ethanoyl chloride, AlCl₃ iii. H₂CrO₄, heat
 D. i. Br₂ / FeBr₃ ii. Mg iii. H₃O⁺ iv. HNO₃ / H₂SO₄
 E. i. HNO₃ / H₂SO₄ ii. Br₂ / FeBr₃ iii. CO₂, H⁺ workup

40.



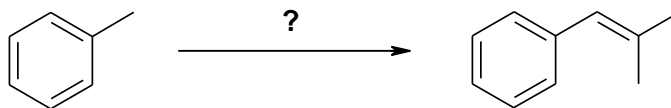
- A. i. Na / NH₃, ii. OsO₄ / t-butylperoxide / aq. NaOH
 B. i. Na / NH₃, ii. aq. H₂SO₄
 C. i. Na / NH₃, ii. CH₃CO₃H iii aq. H₂SO₄
 D. i. H₂ / Lindlar's catalyst, ii. KMnO₄ / aq. NaOH / 0°C
 E. i. H₂ / Lindlar's catalyst, ii. CH₃CO₃H iii CH₃OH / H₂SO₄

41.



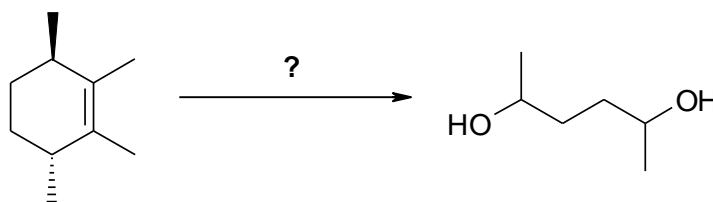
- A. i. LiAlH₄ then H⁺ workup ii. 1,2-ethanediol / TsOH iii. aq. H₂SO₄, heat
 B. i. aq. H₂SO₄, heat ii. 1,2-ethanediol / TsOH iii. LiAlH₄ then H⁺ workup
 C. i. excess LiAlH₄ then H⁺ workup ii. excess PDC / CH₂Cl₂
 D. i. 1,2-ethanediol / TsOH ii. LiAlH₄ then H⁺ workup iii. aq. H₂SO₄, heat
 E. i. 1,2-ethanediol / TsOH ii. NaBH₄ iii. KOH, heat

42.



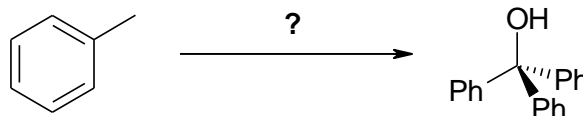
- A. i. HCl, peroxides ii. $P(Ph)_3$ iii. *n*-BuLi iv. 2-propanone
B. i. NBS, $CHCl_3$ ii. $P(Ph)_3$ iii. *n*-BuLi iv. 2-propanone
C. i. NBS, $CHCl_3$ ii. Mg iii. 2-bromopropane
D. i. NBS, $CHCl_3$ ii. Mg iii. 2-bromopropane iv. H_2SO_4 , heat
E. i. $KMnO_4 / H^+ /$ heat ii. $LiAlH_4$ then H^+ workup iii. PBr_3 iv. 2-propyl-MgBr

43.



- A. i. $KMnO_4$, KOH, $0\text{ }^\circ\text{C}$ ii. HIO_4 iii. excess MCPBA iv. aq. HCl, heat
B. i. O_3 ii. dimethyl sulfide iii. $NaBH_4$
C. i. O_3 ii. dimethyl sulfide iii. $LiAlH_4$ then H^+ workup, iv. H_2SO_4 , heat
D. i. O_3 ii. H_2O_2 iii. $LiAlH_4$ then H^+ workup
E. i. MCPBA ii. H_3O^+ iii. HIO_4 iv. $NaBH_4$

44.



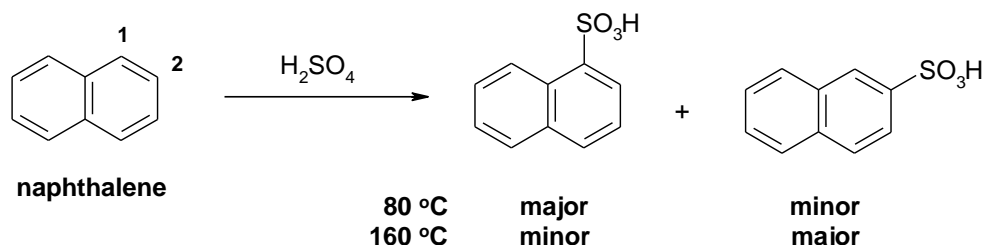
- A. i. NBS, CH_2Cl_2 ii. Mg iii. excess benzyl bromide iv. H_3O^+ workup
B. i. NBS, CH_2Cl_2 ii. Mg iii. methyl benzoate iv. H_3O^+ workup
C. i. $KMnO_4 / H^+ /$ heat ii. MeOH / H_3O^+ , heat iii. excess PhMgBr, H_3O^+ workup
D. i. PDC, CH_2Cl_2 ii. excess PhMgBr iii. H_3O^+ workup
E. i. $KMnO_4 / H_2SO_4 /$ heat ii. MeOH / H_3O^+ , heat iii. excess benzoic acid

7.5% **PART 6: EXPLANATION OF PHENOMENA**

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 45 - 50.

CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

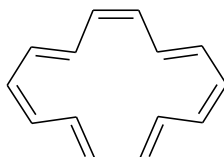
45. The sulfonation of naphthalene was carried out at two different temperatures, 80°C and 160°C. Both temperatures produced the same two products, except the relative distribution of products were different, as shown below.



The 1-sulfonation product is favoured at low temperatures because:

- A. High temperatures cause carbocation rearrangements
- B. Low temperatures direct to the 1-position of polycyclic aromatics
- C. There is steric crowding around the SO₃H group
- D. The cation intermediate is more stable
- E. The cation intermediate is of higher energy

46. [14]-annulene is not aromatic. This is because

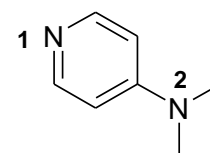


- A. The planar conformation is less stable because it contains 14 π electrons.
- B. Conjugation destabilises the planar conformation.
- C. It is anti-aromatic because it violates the Huckel (4n + 2) rule.
- D. Steric effects destabilise the planar conformation.
- E. Since it contains 14 π electrons, it violates the Huckel (4n + 2) rule.

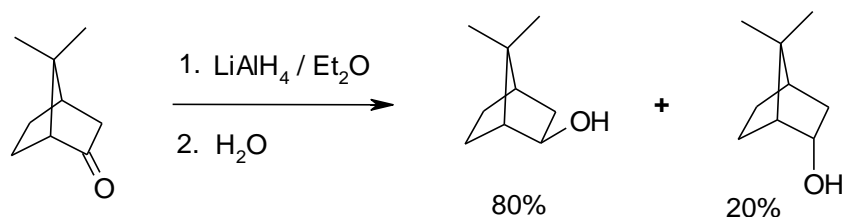
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47. Dimethylaminopyridine has two basic nitrogen atoms labeled as **1** and **2** (shown below). Which N atom is more basic any why?

- A. N1 because the N1 lone pair is in an sp^2 hybrid orbital
- B. N1 because it's conjugate acid is resonance stabilised.
- C. N2 because the N2 lone pair is in an sp^2 hybrid orbital
- D. N2 because the N2 lone pair is in an sp^3 hybrid orbital
- E. N2 because it's conjugate acid is resonance stabilised.



48. The following ketone reacts with $LiAlH_4$ with the stereochemistry shown below. This is because:



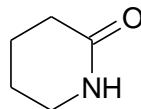
- A. Substituents tend to prefer equatorial positions on cyclohexane ring systems.
- B. There is less steric hinderance if the nucleophile attacks from the top face.
- C. There is less steric hinderance if the nucleophile attacks from the bottom face.
- D. There is less steric hinderance if the electrophile attacks from the top face.
- E. There is less steric hinderance if the electrophile attacks from the bottom face.

49. In electrophilic aromatic substitution reactions of the following systems.



- A. The substituents in **X** and **Y** are both *ortho* / *para* directors.
- B. The substituents in **X** and **Y** are both *meta* directors.
- C. The substituent in **X** is an *ortho* / *para* director and in **Y** is a *meta* director.
- D. The substituent in **Y** is an *ortho* / *para* director and in **X** is a *meta* director.
- E. The substituent in **X** is an *ortho* / *para* director and in **Y** is not selective.

50. A chemist attempted to reduce the compound shown below with LiAlH_4 to give 1,5-pentanediol but did not obtain the desired alcohol product. This is because:

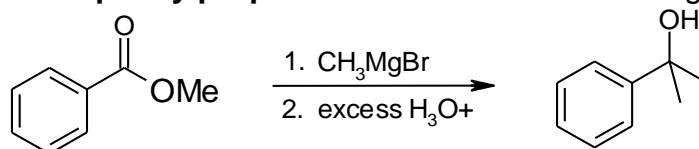


- A. LiAlH_4 is not reactive enough to reduce amides.
- B. LiAlH_4 is not reactive enough to reduce amines.
- C. The actual product is an amino alcohol.
- D. The actual product is an alcohol.
- E. The actual product is an amine.

7% **PART 7: LABORATORY**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

- (3%) Calculate the % yield of 2-phenylpropan-2-ol based on the following experimental data:



Methyl benzoate (2.723g) and methyl magnesium bromide (4.17g) in THF (50mL) were stirred at room temperature. After 45 minutes, the mixture was made acidic with cold dilute aqueous acid. The reaction was cooled and allowed to precipitate. The product was collected by vacuum filtration and dried to give crude 2-phenylpropan-2-ol (2.00g).

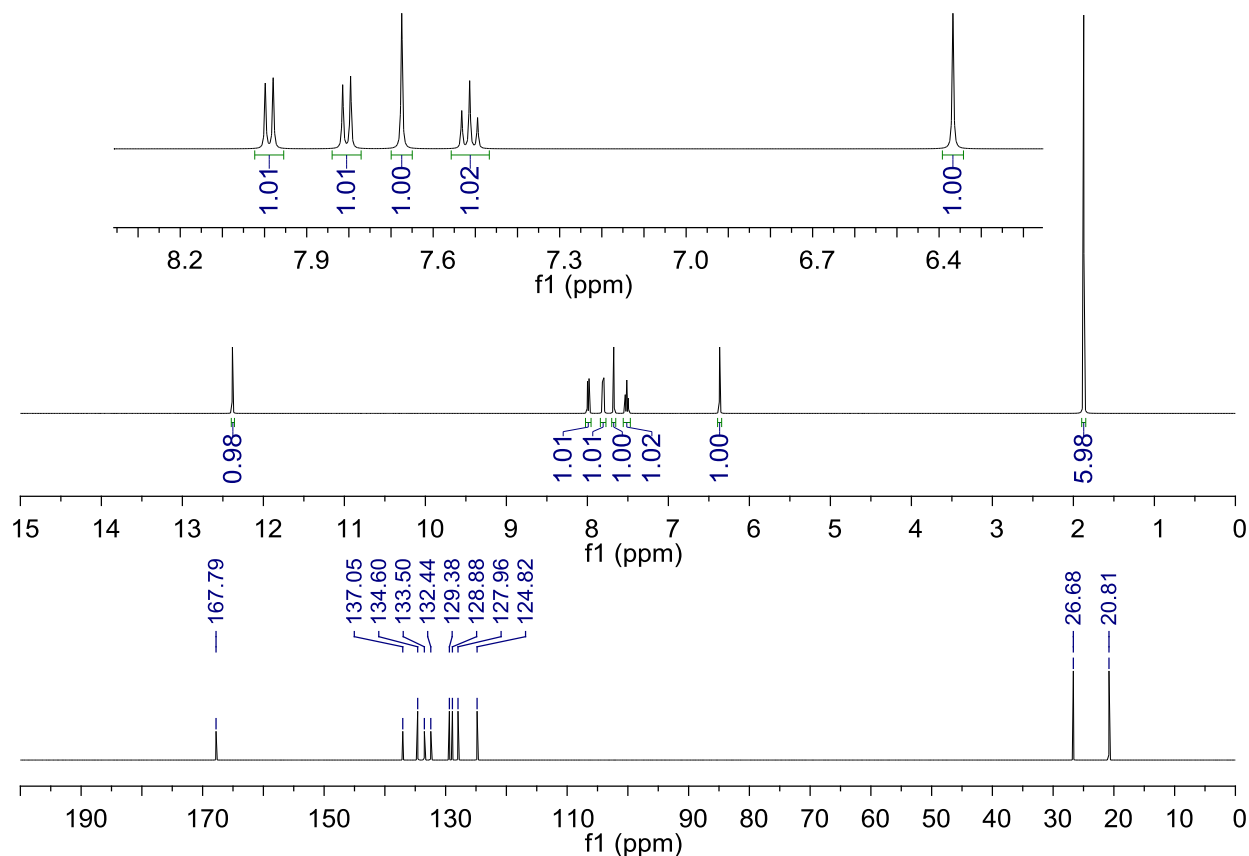
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PART 7: LABORATORY (continued)

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

(4%) The ¹H NMR spectrum of unknown compound #051 and its functional group test results are shown below. In order to answer the question, draw ONE structure that is consistent with the experimental results in your exam booklet.

Compound #051 - C₁₁H₁₂O₂



H-NMR : peak at 12.4 ppm exchanges with D₂O.

Solubility : dissolved in 5% NaHCO₃.

Chemical Test results for compound #051 :

2,4-D.N.P. : no observable colour change

Tollen's: no precipitate formed

FeCl₃: no observable colour change

I₂/KOH : no precipitate formed

Br₂ / CH₂Cl₂ : colourless solution formed

CONTINUED -->

10% **PART 8: MECHANISM**

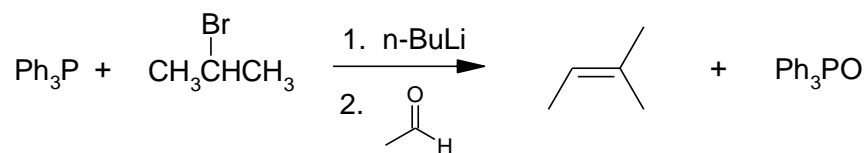
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

ANSWER TWO (2) QUESTIONS, **ONE** from PART A and **ONE** from PART B.

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

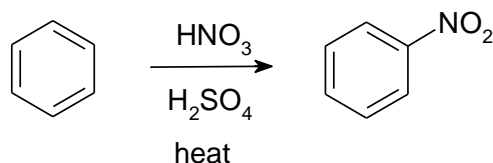
(5%) **PART A: Use a curly arrow mechanism to explain ONE of the following reactions:**

i.



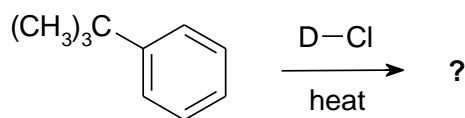
OR

ii.

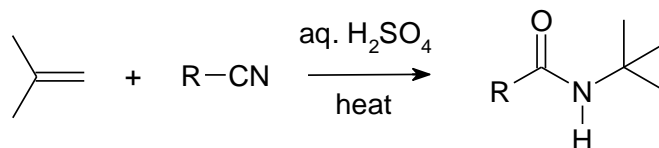


(5%) **PART B: Use a curly arrow mechanism to answer ONE of the following:**

- i. **Show the mechanism** that accounts for the formation the major product of the following electrophilic aromatic substitution reaction (note that D is deuterium, a heavier isotope of hydrogen):



- ii. **Provide a detailed mechanism** showing the steps involved in the following reaction of 2-methylpropene with a nitrile in aqueous H_2SO_4 . This reaction is also known as the Ritter reaction.



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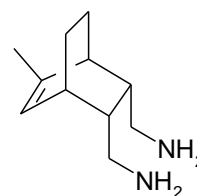
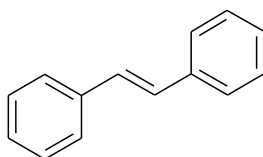
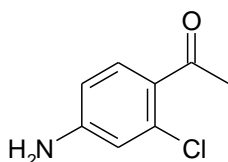
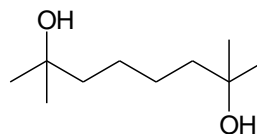
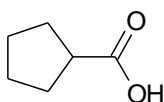
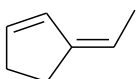
12% PART 9: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Design an efficient synthesis for any **THREE (3)** of the following target molecules using any of the starting materials and reagents given in the accompanying list.

DO NOT SHOW MECHANISMS (*i.e.* curly arrows are **NOT** required)

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED FOR EACH STEP AND THE INTERMEDIATE FORMED FROM EACH REACTION.



Permitted Starting Materials*

- Any organic compounds with no more than **FOUR** carbons
- benzene
- 1-methylcyclohexene

* any materials that contribute carbon atoms to the target molecule *must* come from the permitted starting material list.

You can use any solvents or other reagents for the reactions provided that they do not contribute carbon atoms to the target.

9% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

A, **B** and **C** are isomeric hydrocarbons, $MW = 134.2 \text{ gmol}^{-1}$

Reaction with $\text{KMnO}_4 / \text{H}^+ / \text{heat}$: **A** and **C** reacted but **B** did not.

Relative rates of reaction with NBS / heat : **C** > **A** > **B** (**B** reacted very slowly compared to **A** and **C**).

When **A** was reacted with NBS / heat or Br_2 / uv , **D** was obtained. When **D** was then heated with KOH to give **E** as a mixture geometric isomers. Reaction of **E** with ozone followed by a work up using zinc / acid gave an equimolar mixture of **I** and **II** whose NMR spectral data is provided below.

When **C** was reacted with NBS / heat or Br_2 / uv , **F** was obtained. When **F** was then heated with KOH to give **G** as a mixture geometric isomers. Reaction of **G** with ozone followed by a work up using zinc / acid gave an equimolar mixture of **III** and **IV** whose NMR spectral data is provided below.

NMR Spectral data:

I H-NMR / ppm : 10.0 (1H,s), 7.5-7.9 (5H, m)
13C-NMR / ppm : 192, 136, 134, 130, 129

II H-NMR / ppm : 9.8 (1H,s), 2.5 (2H, q), 1.1 (3H, t)
13C-NMR / ppm : 203, 37, 6

III H-NMR / ppm : 7.7-7.9 (5H, m), 2.6 (3H, s)
13C-NMR / ppm : 198, 137, 133, 129, 128, 26

IV H-NMR / ppm : 9.8 (1H, s), 2.2 (3H, s)
13C-NMR / ppm : 200, 31

Identify the compounds **A** to **G** and **I** to **IV** (structures are sufficient).

****** THE END ******

PERIODIC TABLE

1 1A																		18 8A
1 H 1.008	2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
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 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95	
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	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 126.9	54 Xe 131.3	
55 Cs 132.9	56 Ba 137.3	57* La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	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)	104 Rf (261)	105 Ha (262)	106 Sg (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)								

Lanthanides *

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
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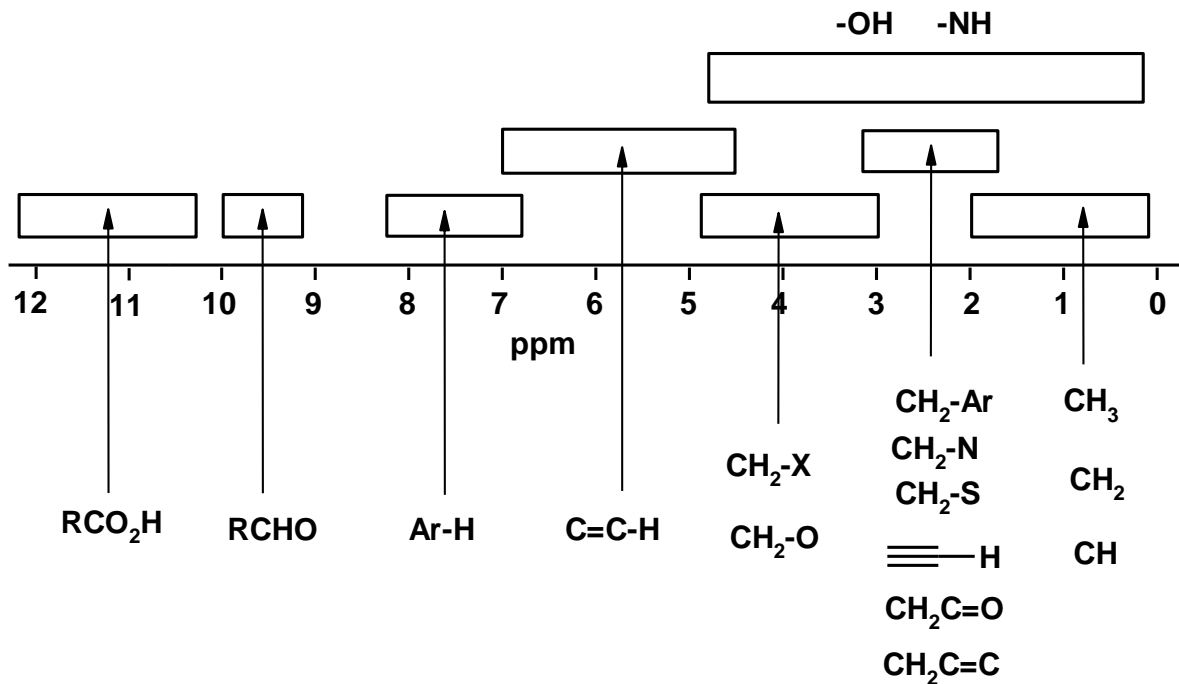
Actinides **

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)
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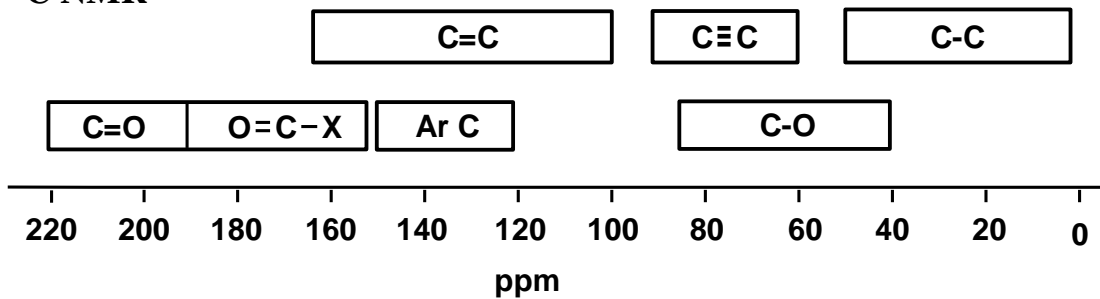
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Schematic diagrams of NMR chemical shift data for H and ¹³C NMR

¹H NMR



¹³C NMR



A Correlation Table of Infra-Red Group Absorption Frequencies

TYPE OF VIBRATION			FREQUENCY (cm ⁻¹)	WAVELENGTH (μ)	INTENSITY
C-H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	-CH ₃	(bend)	1450 and 1375	6.90 and 7.27	m
	-CH ₂ -	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C-C	Alkane	not interpretatively useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810 ca. 1760	ca. 5.52 ca. 5.68	s s
C-O	Alcohols, Ethers, Esters, Carboxylic acids		1300-1000	7.69-10.0	s
O-H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids*		3300-2500	3.03-4.00	m
N-H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro (R-NO ₂)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C-X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(* note that the -OH absorption of carboxylic acids which are solids and run as a nujol mull can be difficult to see as they maybe very broad)