THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 20th, 2007 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 - 7 will be computer graded, and only Parts 8, 9 and 10 are to be answered in the booklet. Parts 1 - 7 consist of a series of multiple choice questions numbered 1 - 62 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.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***. **Absolutely no other electronic devices are allowed.**

Value

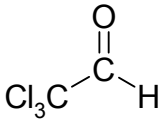
12% **PART 1: RELATIVE PROPERTIES**

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

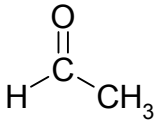
Arrange the items in questions **1-10** in **DECREASING ORDER** (*i.e.* greatest, most etc. first) with respect to the indicated property. Use the following code to indicate your answers:

A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

1. The relative reactivity towards sodium borohydride in ethanol of each of the following:



i



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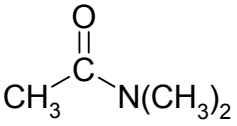
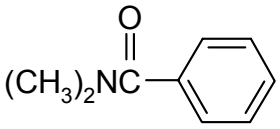
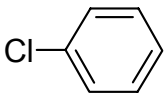


iii

2. The relative reactivity towards Br_2 / $FeBr_3$ of each of the following:



i



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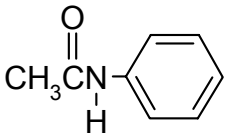
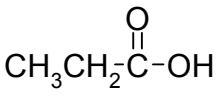
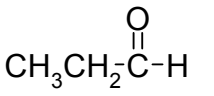


iii

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



i



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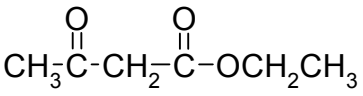
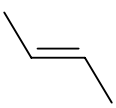


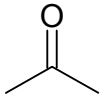
iii

4. The relative strength of the pi bonds in each of the following:



i

ii



iii

5. The relative reactivity towards HCl in $CHCl_3$ of the following:

CH_2=CH-CH_3 CH_2=CH-O-CH_3 CH_2=CH-CO_2CH_3

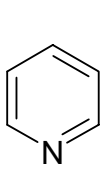
i **ii** **iii**

CONTINUED -->

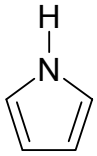
Use the following code to indicate your answers:

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 basicity of each of the following:



i



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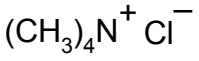
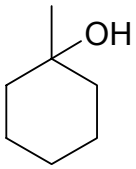
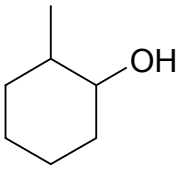


iii

7. The relative yields of the following products from the reaction of (1) $HgSO_4$, aq. H_2SO_4 (2) $NaBH_4$ with 1-methylcyclohexene :



i



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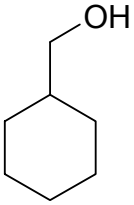

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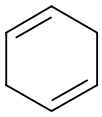
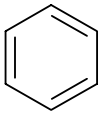
8. The resonance energies of each of the following:



i



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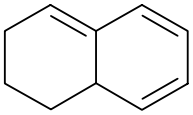


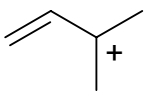
iii

9. The relative reactivity of the following towards propanone in dry THF:

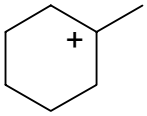
CH_3MgBr CH_3SH CH_3OH

i **ii** **iii**

10. The relative stability of the following systems:



i



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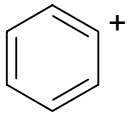

iii

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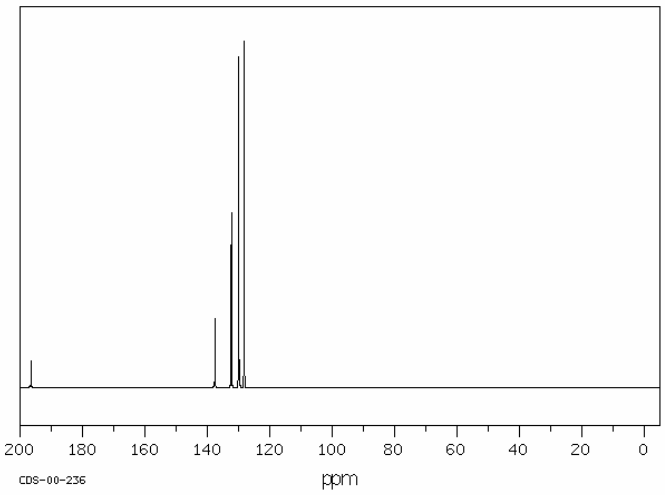
8% PART 2: LABORATORY

ANSWER ALL EIGHT (8) OF THE QUESTIONS 11-18.

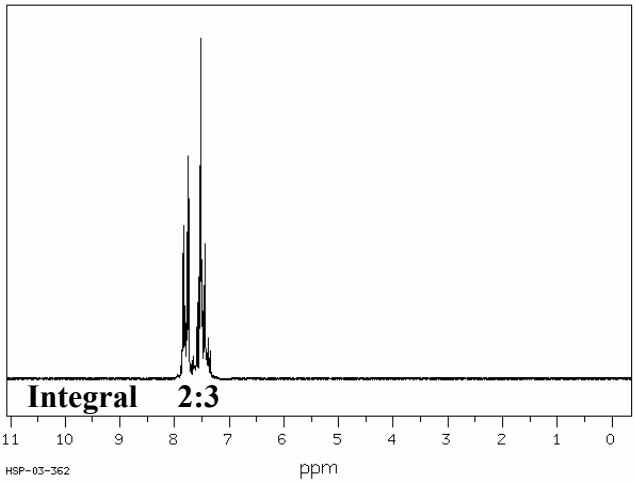
Questions **11-16** relate to the unknowns experiment:

Stu Dent, a student in CHEM 353 here in Calgary, had an unknown **#9999** which is white crystalline solid. The melting point was determined to be 47-48 °C, and the boiling point to be 286-288 °C (uncorrected). ^{13}C and ^{1}H-NMR of **#9999** are shown below.

^{13}C NMR:



^{1}H NMR:



11. The corrected melting point for unknown **#9999** should be approximately:

A 40 °C **B** 44 °C **C** 48 °C **D** 52 °C **E** 56 °C

12. The corrected boiling point for unknown **#9999** should be approximately:

A 276 °C **B** 281 °C **C** 288 °C **D** 295 °C **E** 305 °C

13. Select **all** the solvents that would completely dissolve unknown **#9999**:

A Water **B** 5% $NaHCO_3$ **C** NaOH **D** 5% HCl **E** Diethyl Ether

14. Based on the spectra above, which of the following tests would be **NEGATIVE** for unknown **#9999** ?

A Bromine in chloroform **B** 2,4-Dinitrophenylhydrazine
C Ferric chloride **D** Iodoform **E** Lucas

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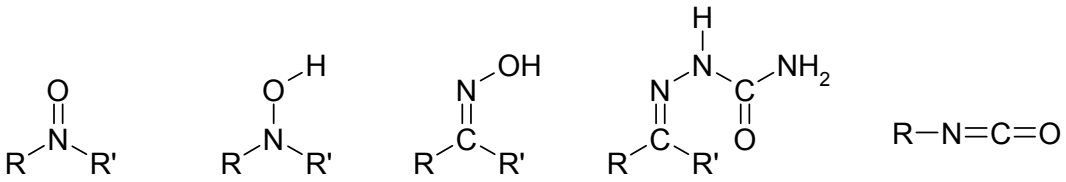
15. The oxime derivative of unknown **#9999** was prepared and found to have a melting point of 195 °C. What is the generic structure of an oxime ?



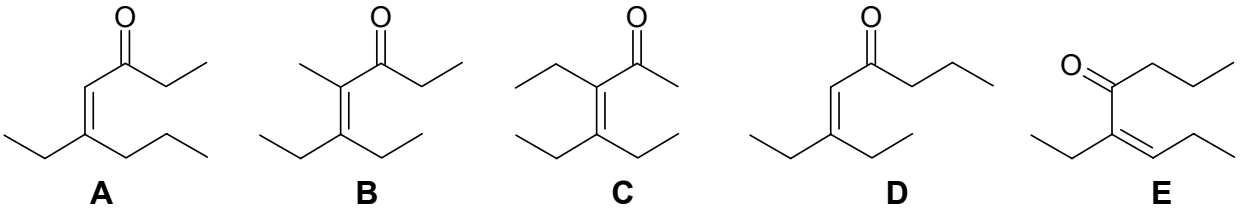
16. Unknown **#9999** gave a negative Tollens test. Based on all the information given, what is the functional group in unknown **#9999** ?

A Alcohol **B** Aldehyde **C** Ester **D** Ketone **E** Carboxylic Acid

Questions **17-18** relate to the Aldol experiment:

17. Select **all** of the following statements about the Aldol experiment that are true:
A The ketone was added to a solution containing the aldehyde and base.
B The reaction can be catalysed by acid
C The electrophile is the enolate ion
D The aldehyde is used in excess
E The base is used in excess

18. Which of the following structures is the product from the self-condensation of two molecules of pentan-3-one ?



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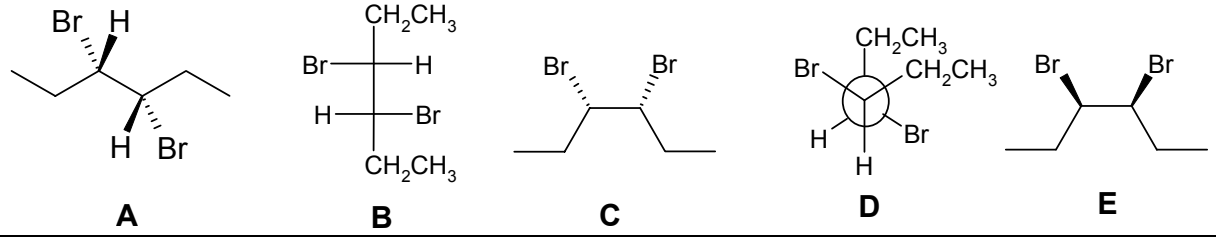
Value

10 % **PART 3: STRUCTURE AND PROPERTIES**

ANSWER ANY TEN (10) OF THE QUESTIONS 19-29.

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

SET 1:



Answer questions **19-22** by selecting the structures from **SET 1** above.

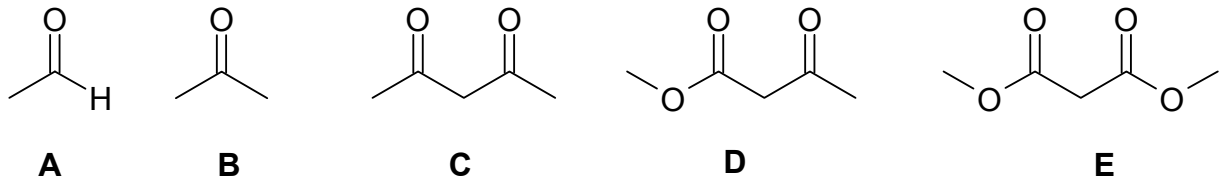
19. Select a structure with an (S,S) configuration

20. Select two structures that are a pair of enantiomers

21. Select two structures that are conformational isomers

22. Select all the structures that represent the product from the reaction of cis-hex-3-ene with bromine in chloroform.

SET 2:



Answer questions **23-26** by selecting the compounds from **SET 2** above.

23. Which compound has the most acidic hydrogen ?

24. Which compound has the greatest number of enolisable hydrogens ?

25. Select all the compounds would be reduced by excess $LiAlH_4$ to give 1,3-propandiol

26. Select all the active methylene compounds

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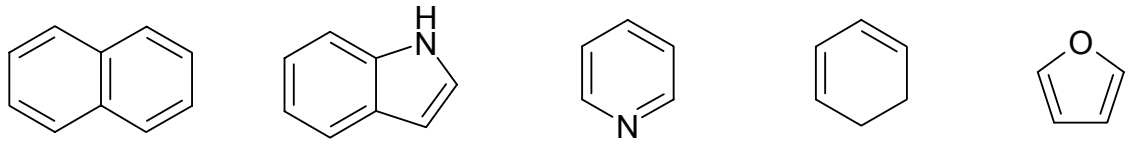
SET 3



A **B** **C** **D** **E**

Answer questions **27-29** by selecting the compounds from **SET 3** above.

27. Select all the systems that are aromatic where n=2 in the Huckel rule

28. Select all the non-aromatic systems

29. Select the most basic heterocyclic aromatic compound

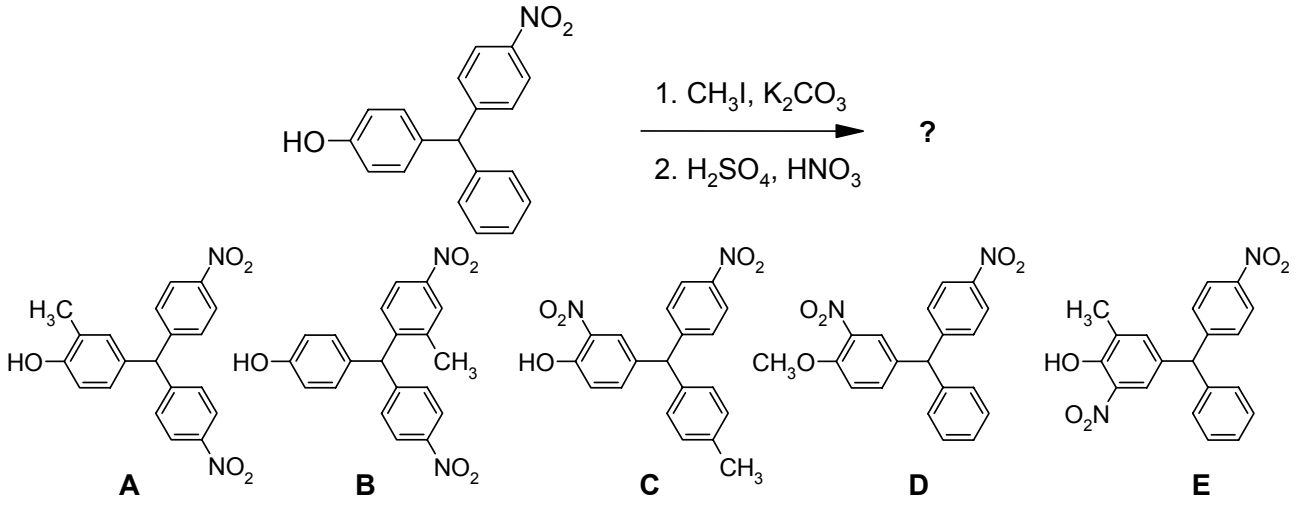
CONTINUED -->

9% **PART 4: PRODUCTS OF SYNTHESIS**

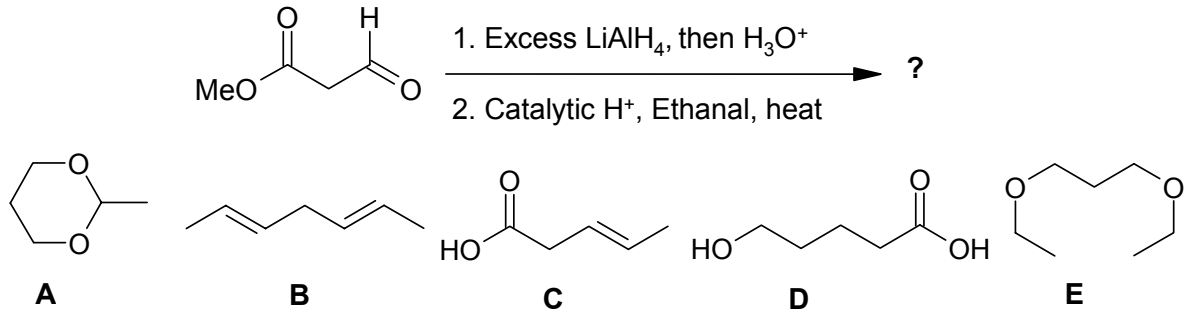
ANSWER ANY SIX (6) OF QUESTIONS 30-36.

For each of the questions **30-36** identify the **major product** obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

30.



31.



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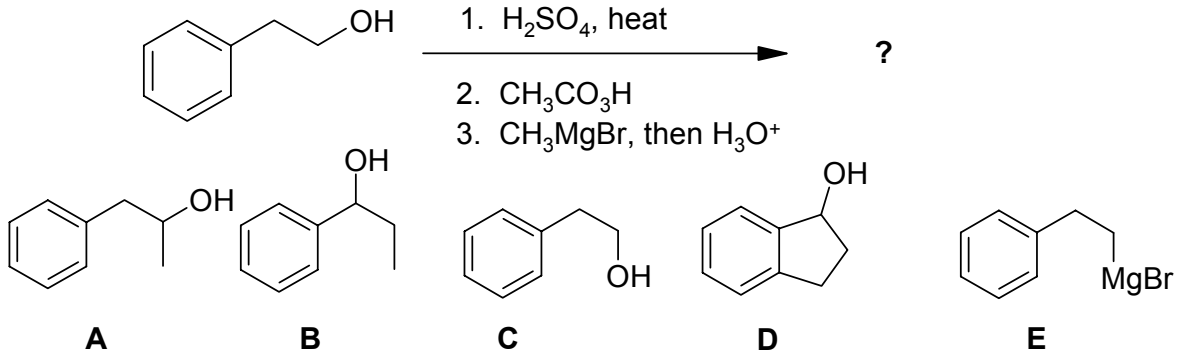

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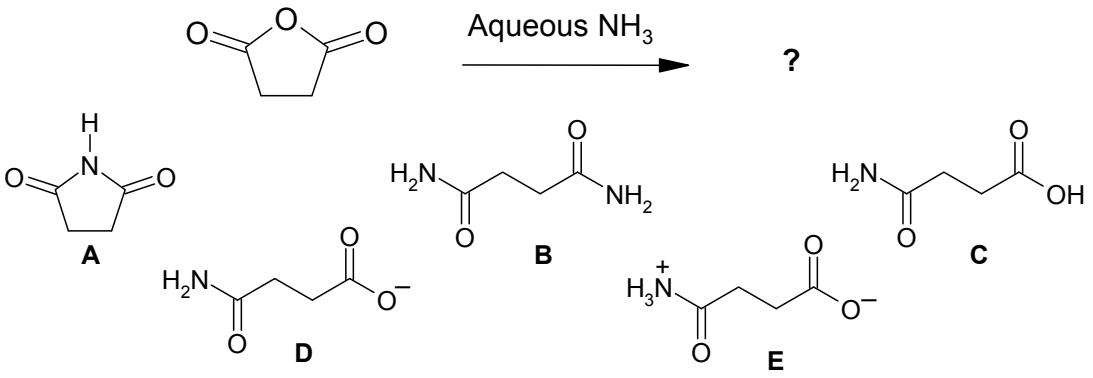
33.



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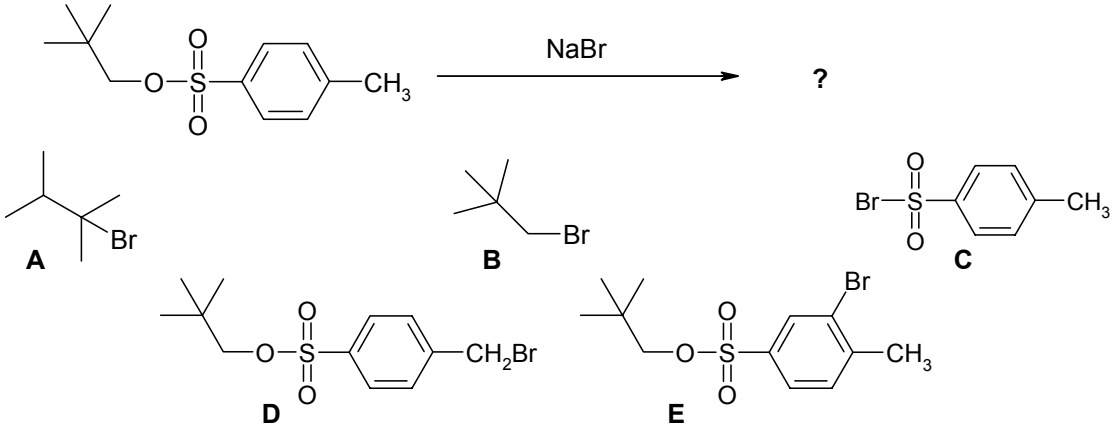

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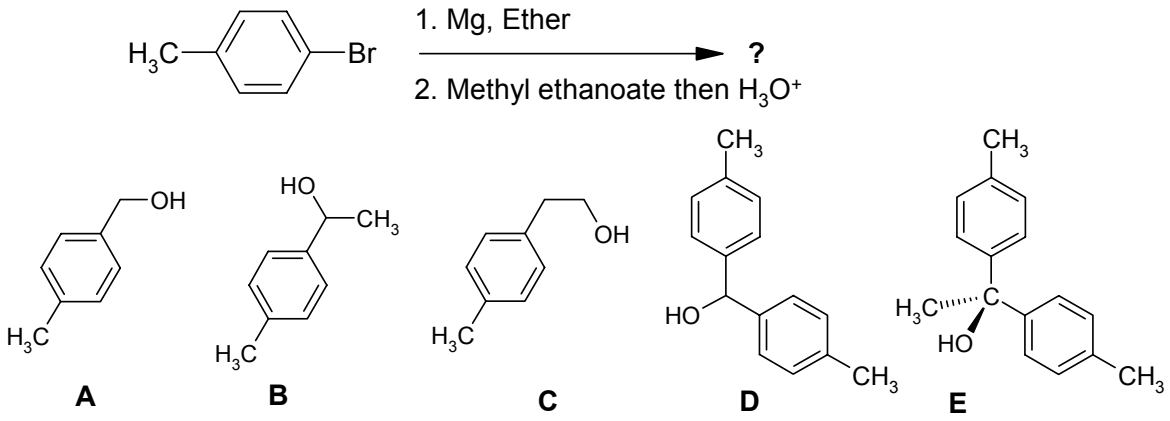

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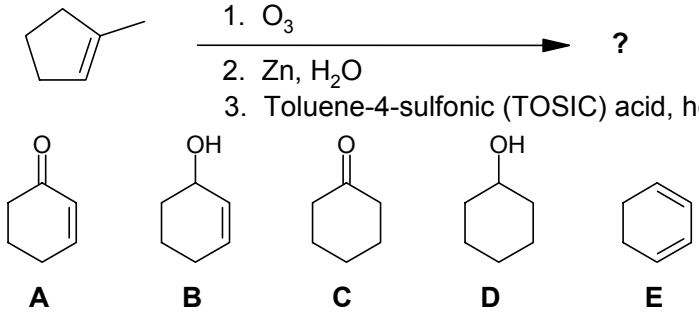

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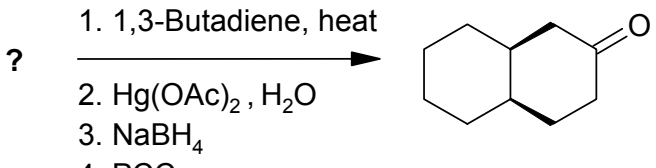
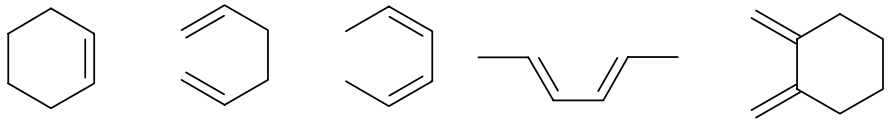
9% PART 5: STARTING MATERIALS FOR SYNTHESIS

ANSWER ANY SIX (6) OF QUESTIONS 37-43.

For each of the questions **37-43**, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

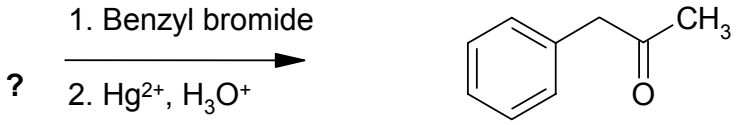
37.

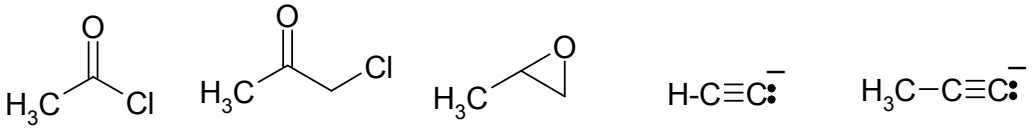




A **B** **C** **D** **E**

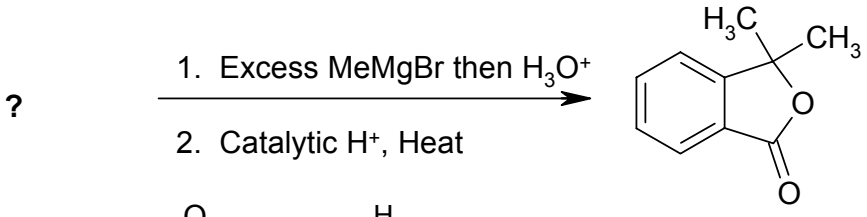
38.

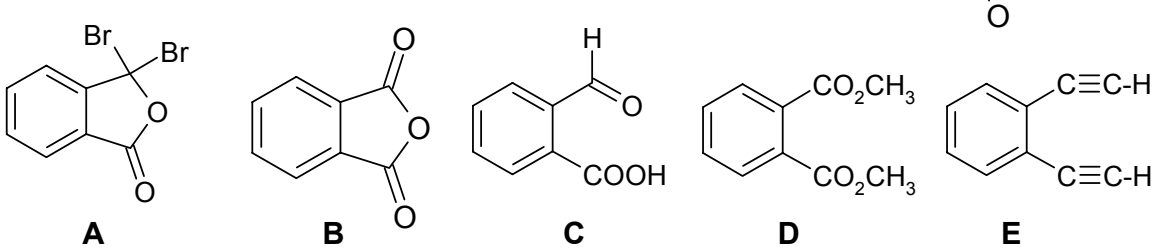




A **B** **C** **D** **E**

39.





A **B** **C** **D** **E**

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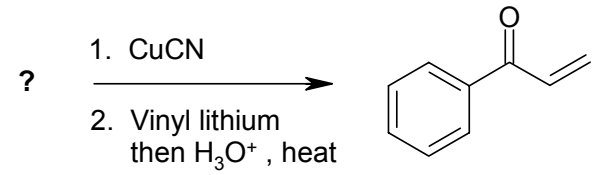
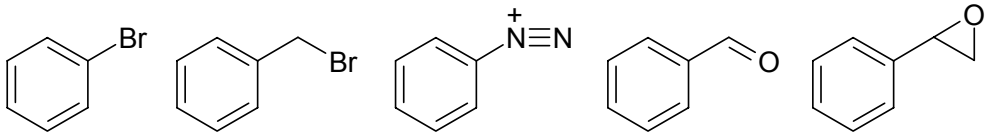
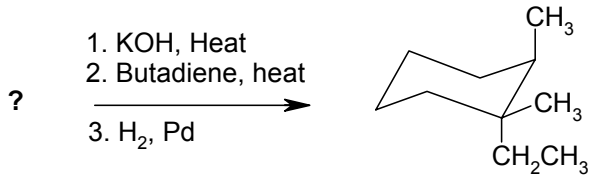
40.

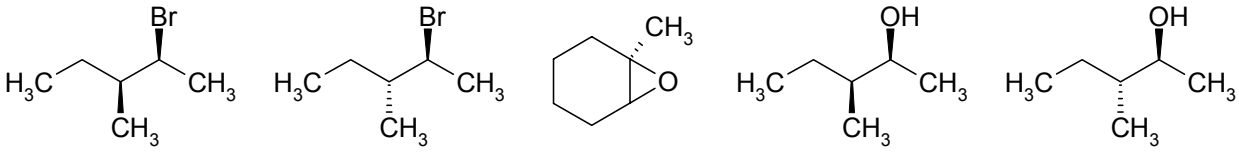




A **B** **C** **D** **E**

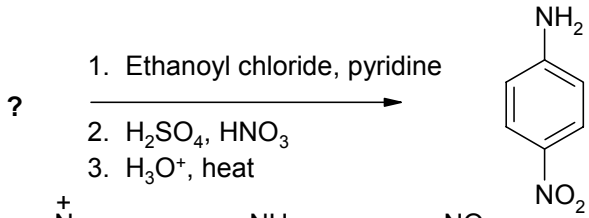
41.

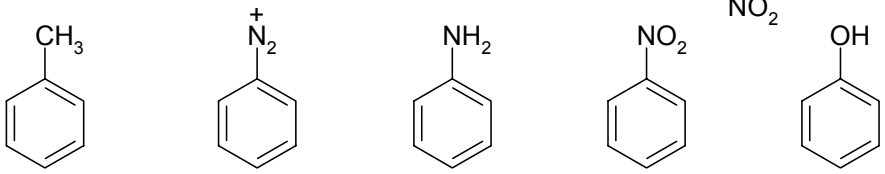




A **B** **C** **D** **E**

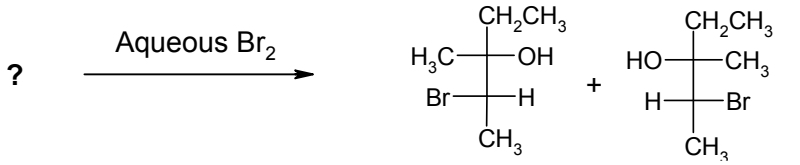
42.



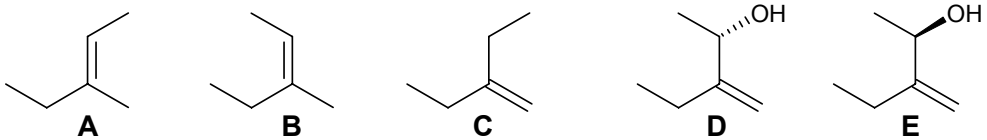


A **B** **C** **D** **E**

43.



(50:50 of these enantiomers)



A **B** **C** **D** **E**

CONTINUED --

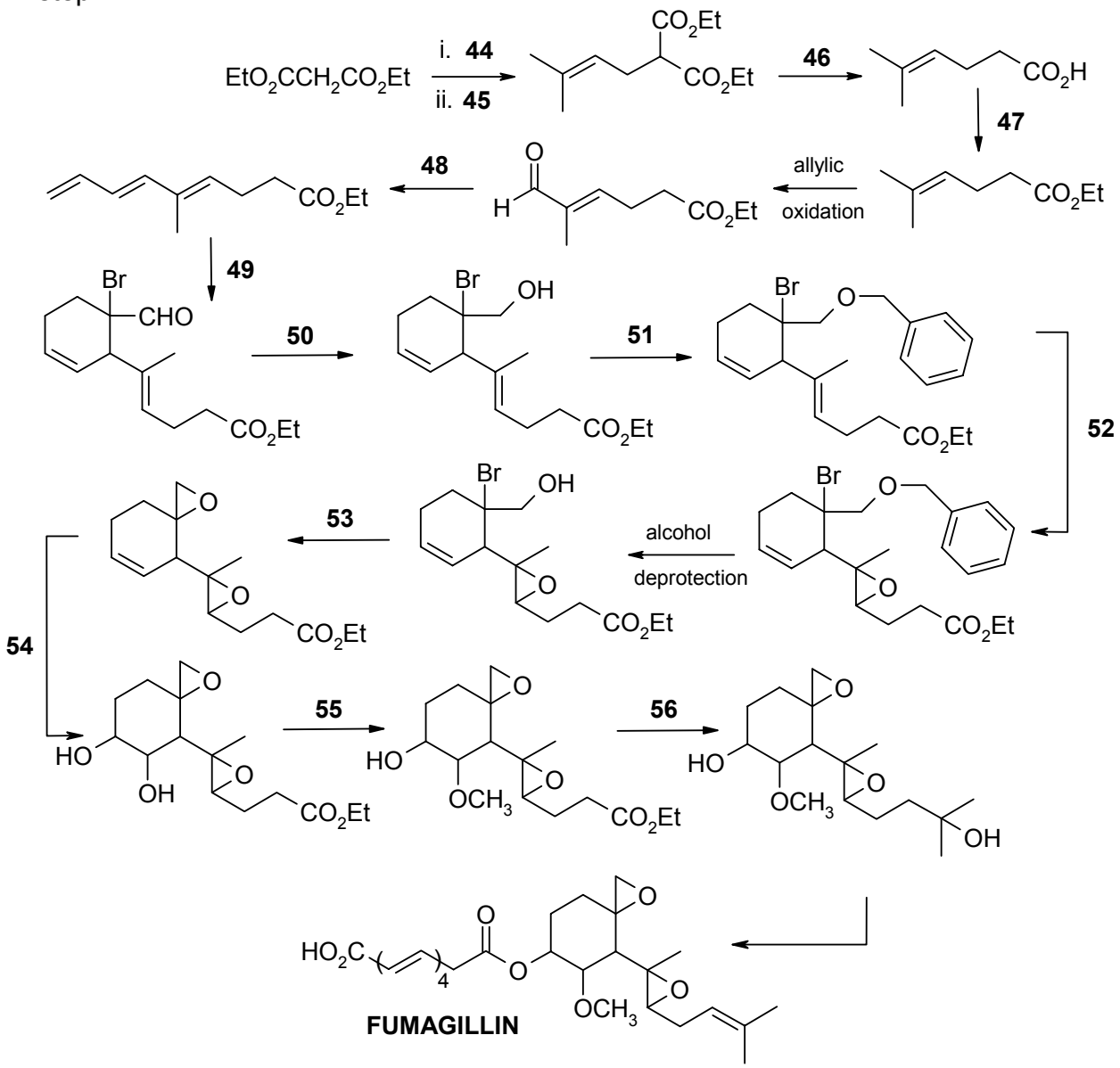
>

Value

13% **PART 6: REAGENTS FOR SYNTHESIS**

ANSWER ALL OF THE QUESTIONS 44 – 56

The reaction scheme below shows the first part of a potential synthesis of the natural antibiotic **FUMAGILLIN**. From the list of reagents provided in the table below, select the best reagent combination to carry out each of the reactions required at each numbered step.



A. CH_2=C(Br)CHO / heat	**AE**. $(CH_3)_2C$=$CHCH_2Br$
B. $NaOCH_2CH_3$ / CH_3CH_2OH	**BC**. CH_3CH_2OH / H+ / heat
C. CH_3CO_3H	**BD**. NaOtBu then CH_3I
D. Ph_3P=$CHCH$=CH_2	**BE**. H_3O^+ / heat
E. Ph_3P=CH_2	**CD**. NaOH / H_2O / heat
AB. PPh_3 then BuLi	**CE**. $LiAlH_4$ / THF then H_3O^+
AC. 2 eq. CH_3Li then H_3O^+	**DE**. $NaBH_4$ / THF then H_3O^+
AD. Na then $C_6H_5CH_2Br$	**ABC**. OsO_4 / tBuOOH

Value

9% **PART 7: EXPLANATION OF PHENOMENA**

ANSWER ALL OF THE QUESTIONS 57 - 62.

CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

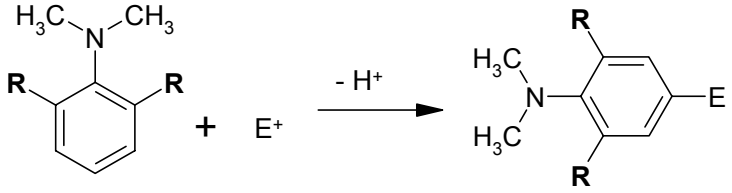
57. When phenylethene is reacted with HBr / peroxides the major product of the reaction is 2-bromo-1-phenylethane. THIS IS BECAUSE:

A H^+ adds to the alkene first to give the most stable carbocation.
B Br^+ adds to the alkene first to give the most stable carbocation.
C An H radical adds to the alkene first to give the most stable radical.
D A Br radical adds to the alkene first to give the most stable radical.
E Br^- adds to the alkene first to give the most stable carbanion.

58. Butanal has a heat of combustion of -2475 kJ / mol, butanone has a heat of combustion of -2442kJ / mol. This is because:

A. Butanal has stronger inter-molecular forces (dipole-dipole and van der Waals).
B. Butanone contains more atoms.
C. Butanal is more flammable.
D. The carbonyl of butanone is attached to more electron releasing groups.
E. Butanone can form an enol more readily.

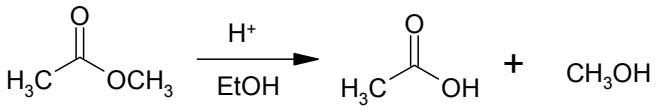
59. For the following reaction, when **R** = H the reaction is fast, but when **R** = CH_3 the reaction is slow:



A When **R** = CH_3, the cationic intermediate is destabilized by inductive effects.
B When **R** = CH_3, the final deprotonation step is slowed down by inductive effects.
C When **R** = CH_3, steric hinderance prevents overlap of the pi-electrons.
D When **R** = H, there is less steric hinderance for electrophilic attack.
E When **R** =H, the cationic intermediate is stabilized by hydrogen bonding.

CONTINUED -->

60. Stu Dent, a student in CHEM 353 attempted the following reaction using toluene-4-sulfonic (TOSIC) acid as an acid catalyst in ethanol solvent: The reaction did not work as drawn because:

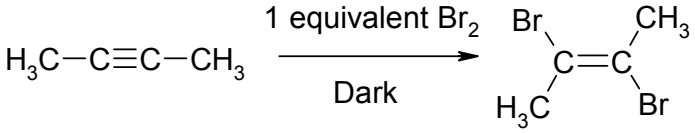


A Toluene-4-sulfonic acid is not soluble in the ethanol solvent.
B This reversible reaction favours starting materials.
C Products were formed, but one of the products is the alkoxide ion.
D No products were formed, because esters can only be hydrolysed by base.
E Ethyl ethanoate was formed as the major product.

61. The boiling point of cyclopentane is 49 °C and the boiling point of tetrahydofuran is 65 °C.

A Ethers have a larger dipole moment, and therefore have greater intermolecular interactions.
B Alkanes have a larger dipole moment, and therefore have greater intermolecular interactions.
C The five membered ring in cyclopentane has more strain.
D The five membered ring in tetrahydrofuran has more strain.
E Tetrahydrofuran can act as a hydrogen bond donor and acceptor.

62. Explain why (E)-2,3-dibromobut-2-ene is the major product in the following reaction:



A Trans double bonds are generally more stable than cis.
B The reaction intermediate involves a vinyl cation.
C The reaction intermediate involves a cyclic bromonium ion.
D The reaction intermediate involves a radical cation.
E The two bromine atoms add in a concerted manner.

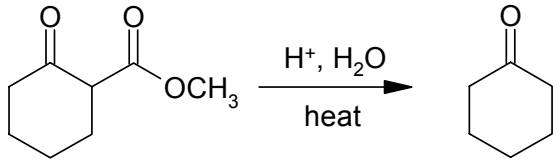
CONTINUED -->

8% PART 8: MECHANISM

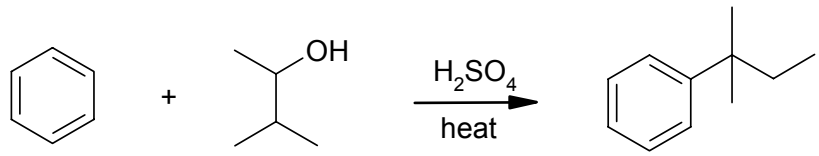
ANSWER TWO(2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B.
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.
NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

(4) PART A: Draw the curly arrow mechanism for ONE of the following transformations:

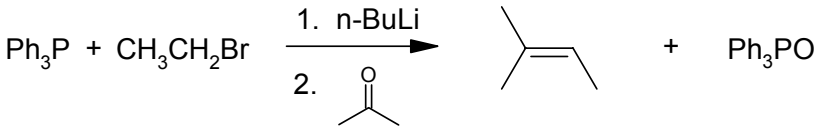
i



ii

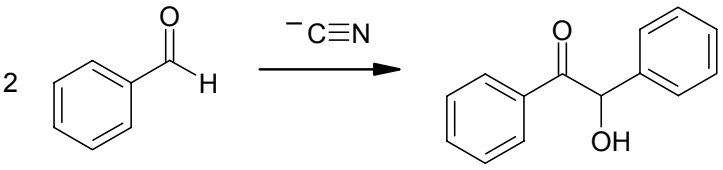


iii

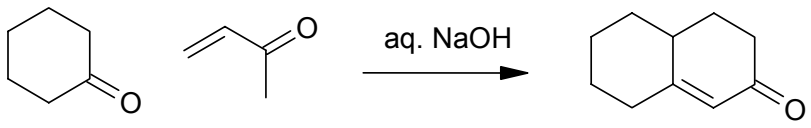


(4) PART B : Draw the curly arrow mechanism for ONE of the following transformations:

i. When benzaldehyde is reacted with cyanide, the product shown to the right can also be formed. A key intermediate is a resonance stabilised carbanion acting as a nucleophile in a aldol like condensation. **Propose a mechanism for this reaction.** *(FYI :it's a benzoin condensation)*



ii. Provide a detailed mechanism showing the steps involved in the following reaction that involves the reaction of an enolate in a conjugate addition (or 1,4-addition) to an enone then an aldol type condensation reaction *(FYI : it's a Robinson annulation) :*



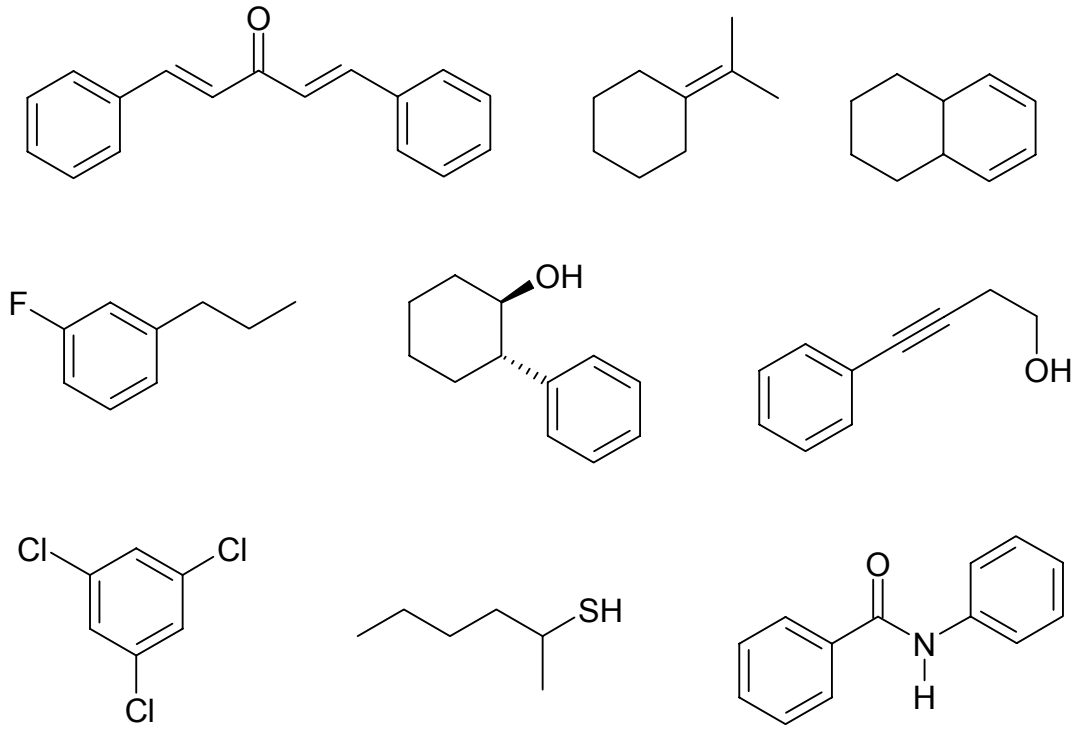
CONTINUED -->

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. **Show the product of each step** and clearly identify the required reagents.

DO NOT SHOW MECHANISMS



Permitted Starting Materials and Reagents (NOTE: any materials that contribute carbon atoms to the target must come from this allowed list):

- Any inorganic materials
- Any organic compounds with no more than **FOUR** carbons
- Benzene

CONTINUED -->

Value

10% **PART 10: STRUCTURE DETERMINATION**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Elemental analysis of compound **A** gave 71.95% C and 12.08% H, IR absorption: 3400 cm^{-1} (strong broad). When **A** was heated with concentrated sulphuric acid, hydrocarbon **B** was obtained, 13C nmr: 127, 25 and 23 ppm.

When **B** was then reacted with O_3 followed with H_2O_2 work-up it give **C**, IR absorptions: 3400 (broad band), 1710 cm^{-1} (strong). When **C** was dissolved in methanol and refluxed with an acid catalyst, a new sweet smelling compound **D** was obtained, H nmr: 3.69ppm, singlet, 3H; 2.32ppm, triplet, 2H and 1.66ppm, triplet, 2H.

Further reaction involved the treatment of **D** with sodium methoxide in methanol to yield **E**, IR absorptions: 1766 and 1728cm^{-1} (both strong), 13C nmr: 212, 170, 55, 52, 38, 27 and 21 ppm.

Subsequently **E** was reacted first with sodium methoxide then with methyl iodide to give **F.** When **F** was heated with aq. sodium hydroxide, a gas was evolved and **G** was obtained. Reaction of **G** with lithium aluminium hydride followed by the normal aq. acid work-up gave 2-methylcyclopentanol.

Note compounds **A**-**D** are achiral, that **E**, **F** and **G** were obtained as racemic mixtures.

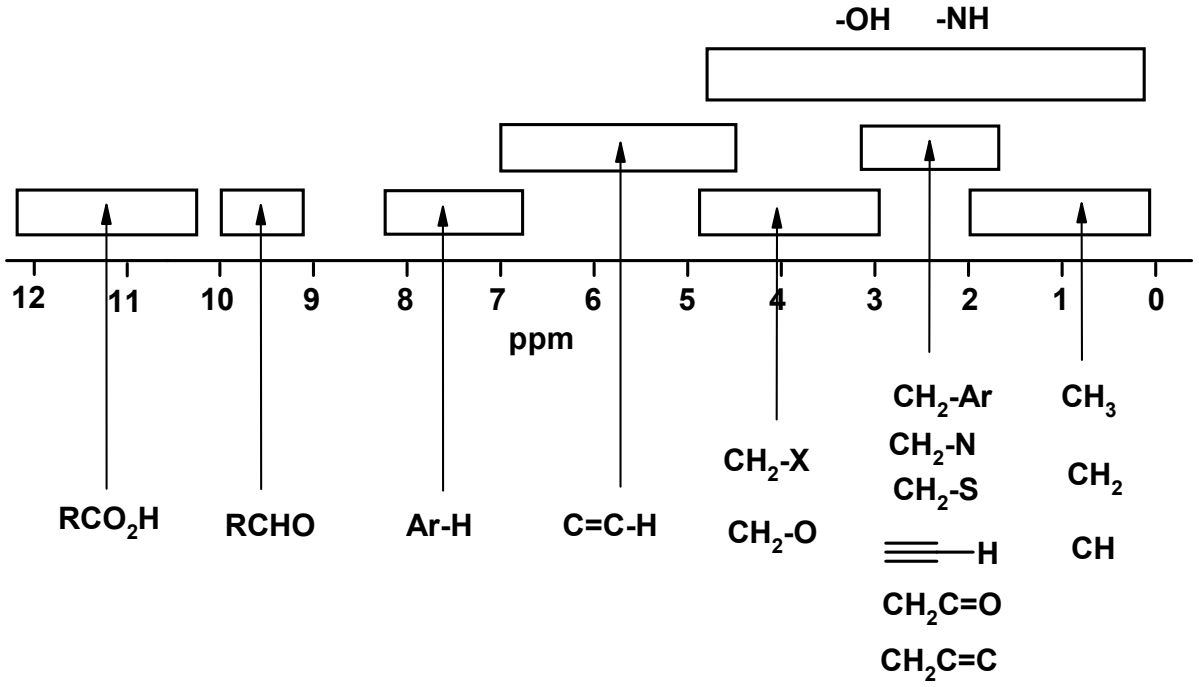
(8.5) Identify the compounds **A**, **B**, **C**, **D**, **E**, **F** and **G** (structures are sufficient)

(1.5) Show the mechanism of how **E** is formed from **D**

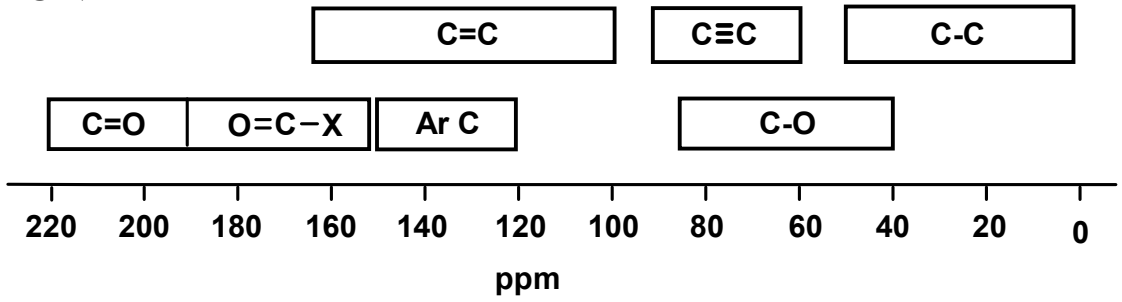
THE END

Schematic diagrams of NMR chemical shift data for H and ^{13}C NMR

^{1}H NMR



^{13}C 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. 5.52	s
			ca. 1760	ca. 5.68	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)

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
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)