UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 18th, 2018

Time: 3 Hours

Version

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME & STUDENT I.D. NUMBER ON <u>BOTH</u> YOUR BLUE ANSWER BOOKLET AND COMPUTER ANSWER SHEET. ENTER VERSION NUMBER 1 ON THE COMPUTER ANSWER SHEET

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 blue answer booklet. Parts **1** - **6** consist of a series of multiple choice questions numbered **1** - **49** which are to be answered on your optical score 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 <u>not ink</u>. In some cases it is required that you indicate <u>multiple</u> 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 <u>both</u> space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased <u>cleanly</u>.

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 and calculators are permitted, *<u>but NOT programmable calculators</u>*. Absolutely no other electronic devices are allowed.

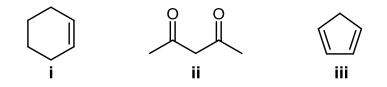
12% PART 1: RELATIVE PROPERTIES

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

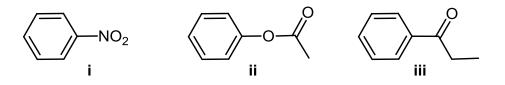
Arrange the items in questions 1-10 in DECREASING ORDER (*i.e.* greatest, most *etc. first*) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

Α	i > ii > iii	D	ii > iii > i
В	i > iii > ii	Е	iii > i > ii
С	ii > i > iii	AB	iii > ii > i

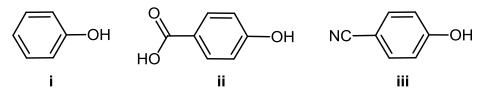
1. The relative acidity of the most acidic hydrogen in each of the following:



2. The relative rate of reaction of Br_2 / Fe with each of the following:



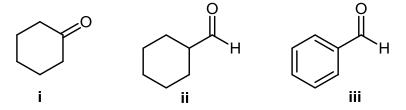
3. The relative acidity of the most acidic hydrogen in each of the following:



4. The relative reactivity of each of the following towards H₂SO₄:

 $\begin{array}{ccc} \mathsf{CICH}=\mathsf{CH}_2 & \mathsf{CH}_3\mathsf{OCH}=\mathsf{CH}_2 & \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}=\mathsf{CH}_2 \\ \mathbf{i} & \mathbf{ii} & \mathbf{iii} \end{array}$

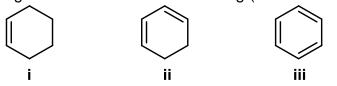
5. The relative acidity of the most acidic hydrogen in each of the following:



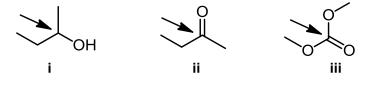
Use the following code to indicate your answers in the box provided:

Α	i > ii > iii	D	ii > iii > i
В	i > iii > ii	Е	iii > i > ii
С	ii > i > iii	AB	iii > ii > i

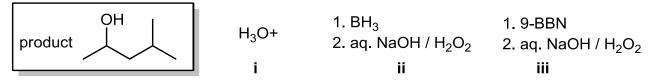
6. The heats of hydrogenation of each of the following (most endothermic first):



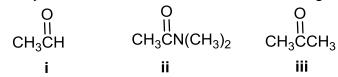
7. The relative oxidation state of the C atom indicated in each of the following:



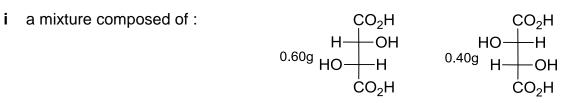
8. The % yield of the alcohol product shown below from the reaction of 4-methylpent-2-ene with each of the following:



9. The relative reactivity towards NaBH₄ of each of the following:



10. The specific rotation of each of the following samples of tartaric acid dissolved in 10mL of the same solvent given that (R,R)-tartaric acid $[\alpha]_D = +12.7$:

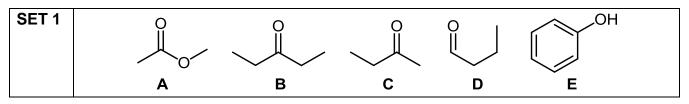


- ii a sample whose observed rotation = 0.635° when 1.0g of tartaric acid was measured in a standard 10cm polarimeter cell
- iii a sample of 1.0 g (2R,3S)-tartaric acid

8 % PART 2: STRUCTURE AND PROPERTIES

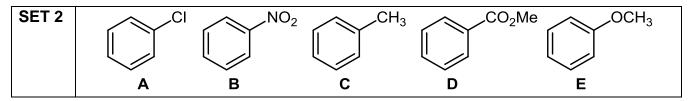
ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 11-19.

IN SOME CASES more than one answer may be correct and ALL compounds that apply MUST be selected for full credit.



Answer questions 11-15 by selecting the compounds from SET 1 above.

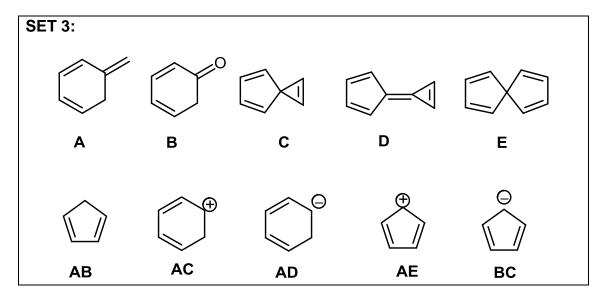
- 11. Which compound has the most acidic hydrogen ?
- **12**. Which **compound(s)** give both a yellow precipitate when tested with 2,4dinitrophenylhydrazine *and* a yellow precipitate when tested with iodoform ?
- **13**. Which **compound(s)** give both a yellow precipitate when tested with 2,4dinitrophenylhydrazine and a silver mirror with Tollen's test ?
- **14**. Which **compound(s)** contain a carbonyl group and give an orange solution with the 2,4dinitrophenylhydrazine test ?
- **15**. Which compound has the **H** with the highest chemical shift in the H-NMR ?



Answer questions 16-19 about electrophilic aromatic substitution by selecting a compound from SET 2 above

- 16. Which compound is the most activated compared to benzene ?
- 17. Which compound is the **most** deactivated compared to benzene ?
- 18. Which compound(s) is/are deactivated and direct meta-?
- 19. Which compound(s) undergo successful Friedel-Crafts alkylation with (CH₃)₃CCI / AlCl₃?

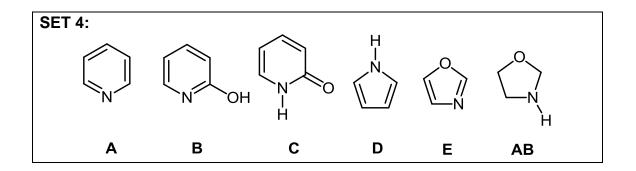
9% PART 3: AROMATICITY AND RESONANCE



ANSWER ANY NINE (9) OF THE TEN (10) QUESTIONS 20 - 29.

Answer questions 20-24 by selecting a <u>SINGLE compound</u> from SET 3 above.

- **20**. Select a **SINGLE** compound that is not aromatic as drawn, but has an aromatic resonance structure.
- 21. Select a **SINGLE** uncharged hydrocarbon that is not aromatic as drawn, but has an aromatic conjugate base.
- 22. Select a **SINGLE** compound that contains an isolated double bond.
- 23. Select a SINGLE compound that is aromatic as drawn.
- 24. Select a **SINGLE** non-aromatic compound that can form an aromatic structure when reacted with a catalytic amount of acid.



Answer questions 25-29 by selecting a <u>SINGLE compound</u> from SET 4 above.

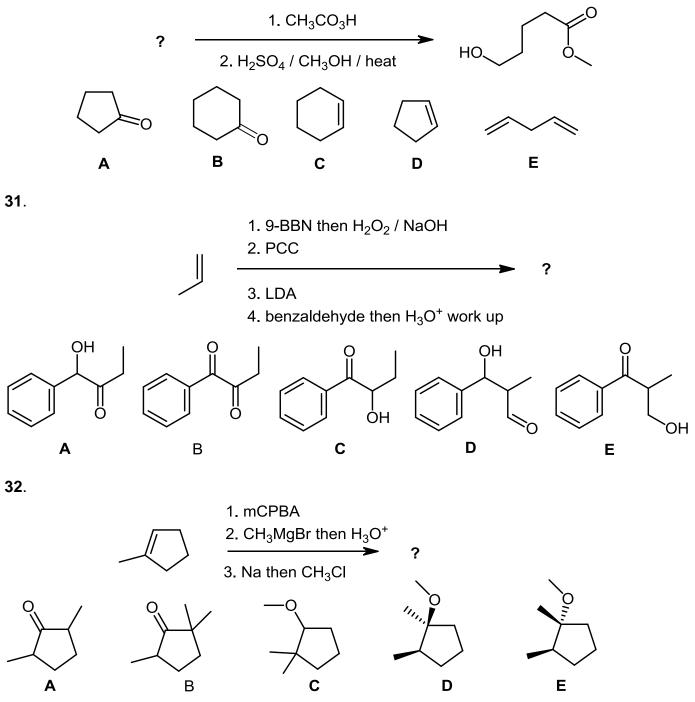
- 25. Select a SINGLE compound that is non-aromatic as drawn but has an aromatic tautomer.
- 26. Select the **SINGLE** compound that is the **weakest** base.
- 27. Select the SINGLE compound that is the strongest base.
- **28**. Select a **SINGLE** compound that has a nitrogen atom with a lone pair of electrons is in an unhybridized p-orbital
- **29**. Select a **SINGLE** compound with the highest resonance energy.

16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

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

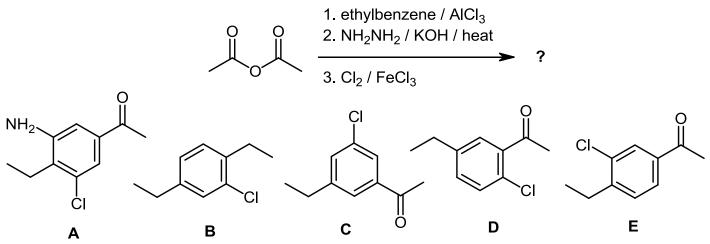
For each of the questions 30 - 38 identify the product(s) obtained or starting material(s) required in order to best complete each of the reaction sequences shown by selecting from the list provided.

30.

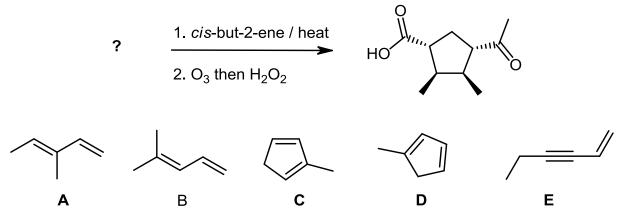


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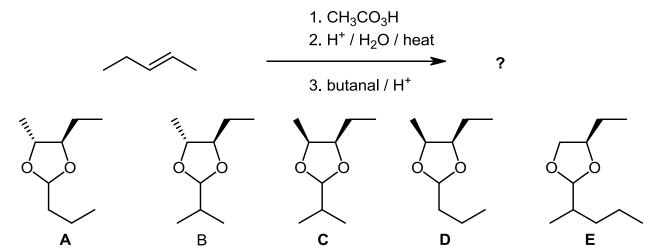
33.



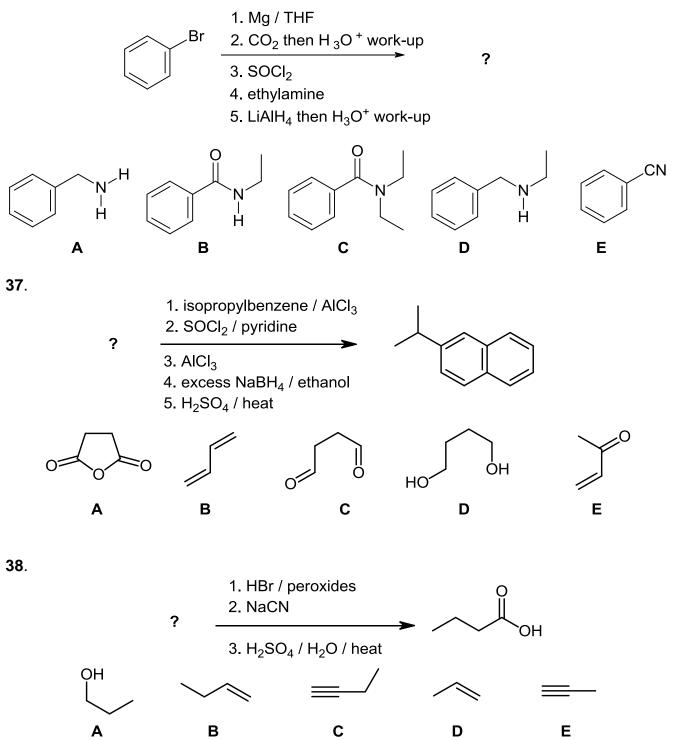
34.



35.



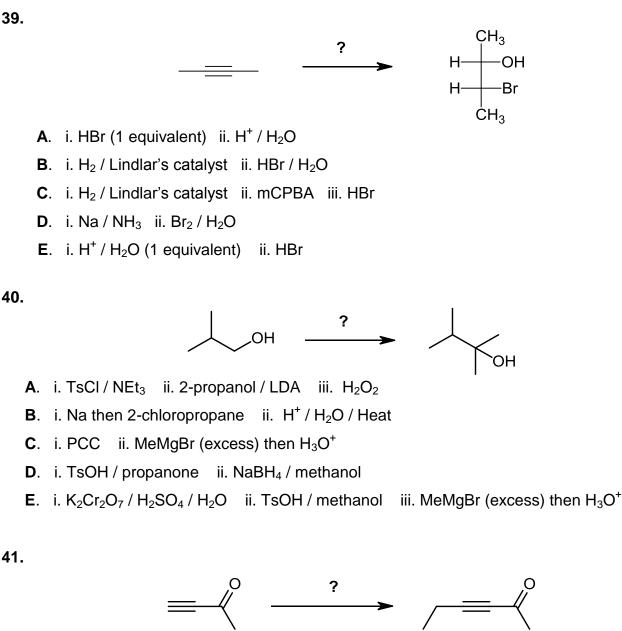
36.



10% PART 5: REAGENTS FOR SYNTHESIS

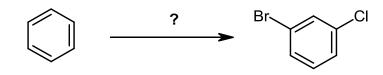
ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 39-44

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



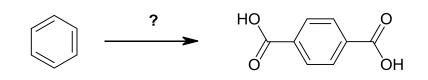
- A. i. NaNH₂ ii. CH₃CH₂Br
- B. i. NaNH₂ ii. CH₃CH₂CH₂Br
- **C**. i. Cl_2 / light ii. CH_3CH_2Br
- **D**. i. NBS ii. CH_3CHO then H_3O^+ work-up
- **E**. i. H^+ / HOCH₂CH₂OH / heat ii. NaNH₂ iii. CH₃CH₂Br iv. H^+ / H₂O / heat

42.



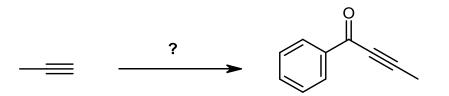
- A. i. $Br_2 / FeBr_3$ ii. $Cl_2 / FeCl_3$
- **B**. i. Cl_2 / FeCl₃ ii. Br_2 / FeBr₃
- C. i. HNO₃ / H₂SO₄ ii. Cl₂ / FeCl₃ iii. Sn / HCl then aq. NaOH iv. NaNO₂ / aq. HCl / cold then CuBr
- D. i. Cl₂ / FeCl₃ ii. HNO₃ / H₂SO₄ iii. Sn / HCl then aq. NaOH iv. NaNO₂ / aq. HCl / cold then CuBr
- E. Br-Cl / NaOH / peroxides / heat

43.



- **A.** i. 2-chloropropane (2 equivalents) / AlCl₃ ii. Na₂Cr₂O₇ / H₂SO₄ / H₂O / heat
- **B.** i. Cl_2 (2 equivalents) / FeCl₃ ii. NaNH₂ iii. CO₂ (excess) then H₃O+
- **C.** i. Cl_2 (2 equivalents) / FeCl₃ ii. Mg / THF iii. ethanoic anhydride then H₃O+
- **D**. i. SO₃ (2 equivalents) / H_2SO_4 ii. CO₂ (excess) then H_3O_+
- **E.** i. CO_2 (2 equivalents) / Fe then H_3O +





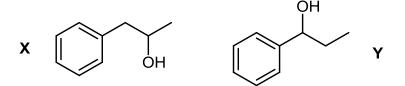
- **A.** i. MeMgBr ii. benzaldehyde then H_3O^+ work-up iii. PCC
- **B**. i. Na / NH₃ ii. methyl benzoate then H_3O^+ work-up
- **C**. i. CI_2 (excess) ii. methyl benzoate then H_3O^+ work-up iii. NaOH / heat
- **D**. i. LDA ii. methyl benzoate then H_3O^+ work-up
- **E**. i. LDA ii. benzaldehyde then H_3O^+ work-up

10% PART 6: EXPLANATION OF PHENOMENA

ANSWER ALL FIVE (5) OF THE QUESTIONS 45 - 49.

Choose the single explanation that best rationalises the phenomenon indicated.

45. 1-Phenylprop-1-ene could react with aq. H₂SO₄ to give either **X** or **Y**. Which is the major product and why ?



- A. X because the H adds end of the alkene with the most H already attached.
- **B**. **X** because H+ adds first to give a benzylic carbocation.
- C. X because HO radical adds first to give a benzylic radical
- D. Y because the H adds end of the alkene with the most H already attached..
- E. Y because the H+ adds first to give a benzylic carbocation.
- **AB**. **Y** because the HO radical adds first to give a benzylic radical.
- **46**. 2-methylpenta-1,4-diene reacts with HBr / dark / N₂ to give one isomer as the major product. Which isomer is the major product and why ?

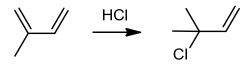


- **A. X** because it has the more stable alkene.
- **B.** X because steric effects destabilise isomer Y.
- **C.** X because it is formed via the more stable radical intermediate.
- **D. Y** because it is the more stable isomer.
- E. Y because it is formed via the more stable carbocation.
- AB. Y because the addition follows Markovinkov's rule.

- **47**. Consider the reaction of nitrobenzene with Br₂ / Fe. Which isomer of bromonitrobenzene is the major product and why ?
 - **A**. ortho because the $-NO_2$ group is activating and o,p-directing.
 - **B**. meta because the $-NO_2$ group is deactivating and m-directing.
 - **C**. para due to steric effects and because the $-NO_2$ is activating and o,p-directing.
 - **D**. ortho because the –Br group is activating and o,p-directing.
 - E. meta because the –Br group is dectivating and m-directing.
 - AB. para due to steric effects and because the –Br is deactivating and o,p-directing.
- 48. Two amides and their pKas for the most acidic hydrogens are shown below. AmideX is more acidic because:

$$\begin{array}{c} X \\ pKa = 15 \end{array} \xrightarrow{O} \\ NH_2 \end{array} \qquad \begin{array}{c} O \\ N(CH_3)_2 \end{array} \qquad Y \\ pKa = 30 \end{array}$$

- A. The conjugate base of **X** is better stabilized by resonance.
- B. The conjugate base of X is better stabilized by an electronegative atom
- C. The conjugate base of Y is better stabilized by resonance
- **D.** The conjugate base of \mathbf{Y} is better stabilized by an electronegative atom
- **E.** The N atom in **X** is sp^2 hybridised.
- **AB.** The N atom in **Y** is sp^3 hybridised.
- **49**. When 2-methylbuta-1,3-diene was reacted with HCl, the major product was as shown below. This indicates that:

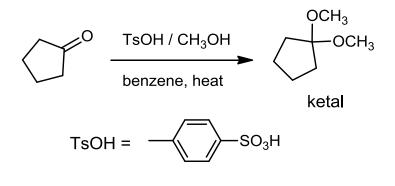


- A. the addition reaction was performed under Markovnikov conditions.
- **B.** the addition reaction was performed under anti-Markovnikov conditions.
- C. the reaction was at lower temperature and under thermodynamic control.
- **D.** the reaction was at lower temperature and under kinetic control.
- E. the reaction was at higher temperature and under thermodynamic control.
- AB. the reaction was at higher temperature and under kinetic control.

5% PART 7: LABORATORY

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

Calculate the % yield of the ketal product based on the following experimental data:



Densities:

Cyclopentanone = 0.95 g/mL

Methanol = 0.79 g/mL

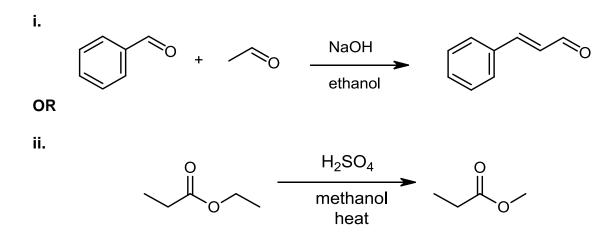
Benzene = 0.88 g/mL

Cyclopentanone (8.412 g), tosic acid (0.1722 g) and methanol (7 mL) were dissolved in benzene (20 mL) and heated at reflux for an hour. The reaction was then cooled in an ice bath and the dimethyl ketal product was collected by distillation, to provide the product (10.00 g).

8% PART 8: MECHANISM

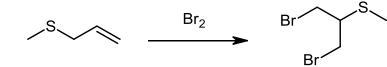
ANSWER TWO (2) QUESTIONS, <u>ONE</u> FROM PART A AND <u>ONE</u> FROM PART B. WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED. NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

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



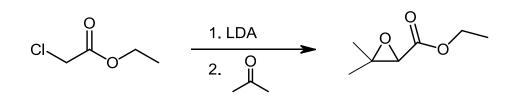
(4) **PART B** : Draw the curly arrow mechanism for ONE of the following transformations:

i.



OR

ii.



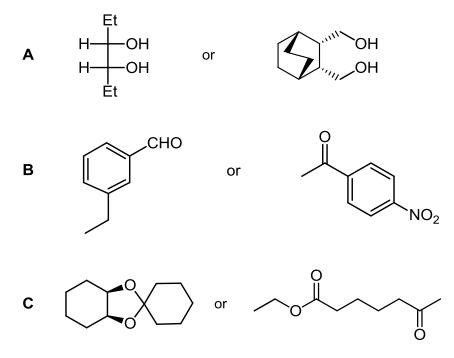
12% PART 9: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

Design an efficient synthesis from the starting materials in the list below for THREE (3) of the following target molecules. Choose ONE target from each of the three sections A, B and C.

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 SYNTHETIC INTERMEDIATE FORMED FROM EACH REACTION.



Permitted Materials and Reagents

<u>NOTE:</u> any materials that contribute <u>carbon atoms</u> to the target molecule must come from this allowed list:

- Any organic compounds with no more than FOUR carbons
- benzene
- cyclohexanol
- You can use any solvents or other reagents for the reactions provided that they do not contribute carbon atoms to the target.

10% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED

A: mass spectra showed $M^{+} = 156$, M+2 = 158; m : m+2 = 1 : 1; ¹³C NMR/ppm: 132,130,127 and 123.

A was reacted with magnesium in THF to which ethylene oxide, C_2H_4O , was then added. After the reaction was complete, dilute acid work up was performed and **B**, $C_8H_{10}O$, was obtained. When characterized, **B** gave the following spectral data: IR absorption 3340 cm⁻¹; H NMR/ppm 7.4-7.1 (5H, multiplet); 3.8 (2H, triplet), 2.8 (2H, triplet) and 2.0 (1H, broad singlet, D₂O exchange)

B was subsequently reacted with PBr_3 / Et_3N and gave compound **C** (mass spectra showed $M^{+} = 184$, M+2 = 186; m : m+2 = 1 : 1).

Treatment of **C** with triphenyl phosphine, PPh_3 , followed by n-butyl lithium gave compound **D** as the major product.

E, C_8H_6 , was reacted with 9-borabicyclononane (also known as 9-BBN) followed by work up with cold aq. alkali hydrogen peroxide to give compound **F**, which gave IR absorption 1724 cm⁻¹. **F** gave a yellow precipitate when reacted with 2,4-DNP and gave a positive Tollen's test. It was later determined that when **B** was reacted with PCC / CH_2Cl_2 it also gave **F**.

When compound **F** was reacted with **D**, compound **G** and triphenyl phospine oxide were obtained.

Reaction of **G** with cold alkali KMnO₄ gave **H** as a single meso compound, IR absorption 3500 cm⁻¹, broad. Reaction of **H** with H_2SO_4 / heat readily gave (1E,3E)-1,4-diphenylbuta-1,3-diene as the major product.

Identify the compounds A to H (structures are sufficient)

THE END

IRH/ASC W2018

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

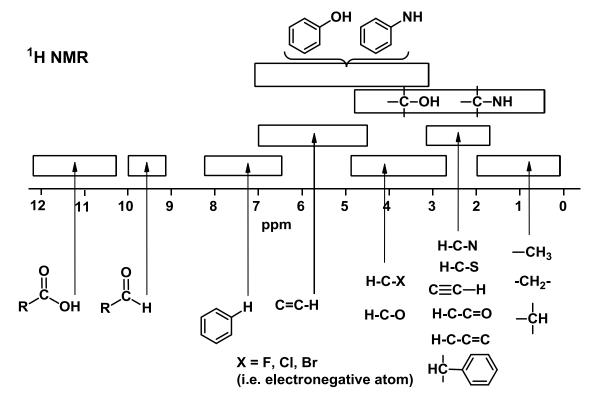
Lr

(260)

PERIODIC TABLE

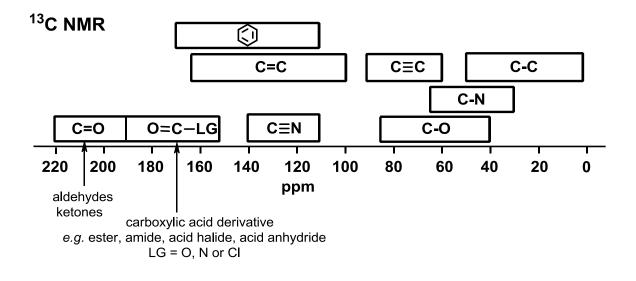
1 1A																	18 8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
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)							
, <u></u>	Lant	hanio	les *	58	59	60	61 B	62 C	63	64	65	66 D	67	68	69	70	71
				Ce 140.1	Pr 140.9	Nd 144.2	Pm (145)	Sm 150.4	Eu 152.0	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0	Lu 175.0

SPECTROSCOPIC TABLES

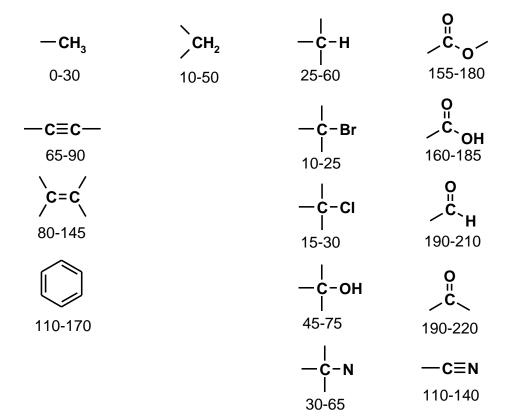


¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

R =	e methyl	methylene	methyne				
	$-CH_3$	-CH ₂ -	–¢н	other			
R-C-	0.9	1.4	1.5	sp ³ C -OH	1-5		
R /				sp ³ C -NH	1-3		
)c=c	1.6	2.3	2.6	С≡сн	2.5		
R R	2.1	2.4	2.5	C=C_H	4.5-6.5		
R-N	2.2	2.5	2.9	н-{	6.5-8		
R	2.3	2.7	3.0	о " R ^{/С} \Н	9-10		
R–Br	2.7	3.3	4.1	o O			
R–Cl	3.1	3.4	4.1	^{к_с} ,он	9-12		
R-0—	3.3	3.4	3.7				



¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

	TY	PE OF VIBRATION	FREQUENCY (cm ⁻¹)	<u>WAVELENGTΗ</u> (μ)	INTENSITY (1)
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 usually 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
	Acyl chloride		1800	5.55	S
C-0	Alcohols, Ethers	s, Esters,			
	Carboxylic acids	8	1300-1000	7.69-10.0	S
O–H	Alcohols, Pheno	bls			
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids	s (2)	3300-2500	3.03-4.00	m
N–H	Primary and see	condary 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
	2'		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, lodide		<600	>16.7	S

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad.