UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 25th, 2011

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 - 52 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 <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 are permitted during the exam; calculators are also permitted, but NOT

programmable calculators.

Absolutely no other electronic devices are allowed.

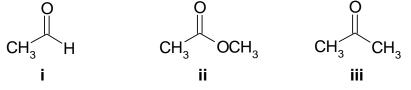
12% PART 1: RELATIVE PROPERTIES

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

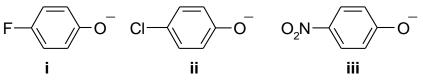
Arrange the items in questions **1-10** in **DECREASING ORDER** (*i.e.* greatest, most etc. first) with respect to the indicated property. Use the following code to indicate your answers:

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

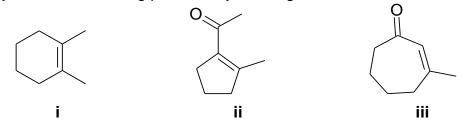
1. The relative pKa of the most acidic hydrogen in each of the following:



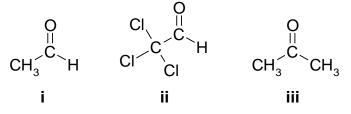
2. The relative basicity of the following phenolates:



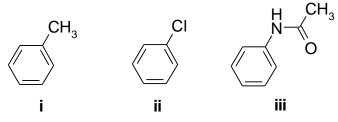
3. The relative yield of the following products by reacting 2,7-octadione with hot KOH:



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



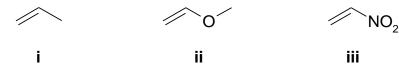
5. The relative reactivity toward Br_2 / FeBr₃ of each of the following:



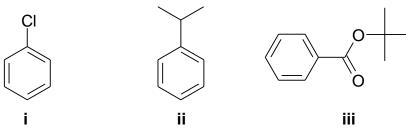
Use the following code to indicate your answers:

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

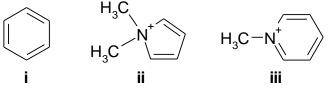
6. The relative reactivity of each of the following towards HCl in CHCl₃:



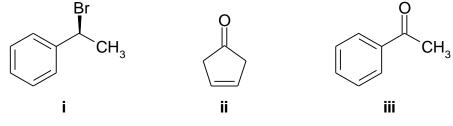
7. The relative yield of the <u>para</u> isomer by reacting each of the following with HNO₃ / H_2SO_4 :



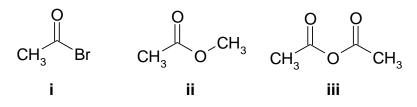
8. The relative resonance energy of each of the following:



9. The number of enolizable in each of the following:



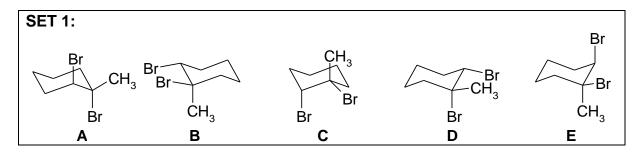
10. The relative rate of hydrolysis by H_2O of each of the following:



10 % PART 2: STRUCTURE AND PROPERTIES

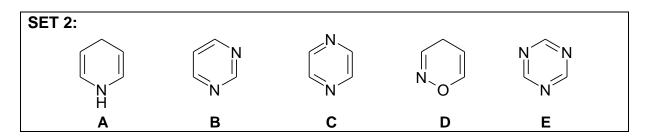
ANSWER ANY TEN (10) OF THE ELEVEN (11) QUESTIONS 11-21.

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** structures that show an equatorial methyl group.
- **12**. Select **TWO** compounds that are identical.
- **13**. Select **ALL** structures that are the result of the reaction of 1-methylcyclohexene with Br_{2} .
- 14. Select **ANY TWO** structures that are a pair of enantiomers.



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

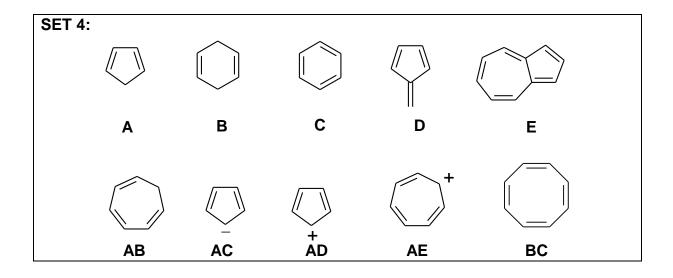
- **15**. Select the structure that contains the **most** basic nitrogen.
- **16**. Select **ONE** structure that is aromatic.
- **17**. Which structure has the **most** peaks in the normal ¹³C NMR?

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

- **18**. Which structure has the **most** enolizable protons ?
- **19.** Which compound has the **most** deshielded peak in the ¹H-NMR spectrum ?
- **20**. Which compound(s) can be used to acylate benzene using $AICI_3$?
- 21. Which compound has the **most** acidic proton ?

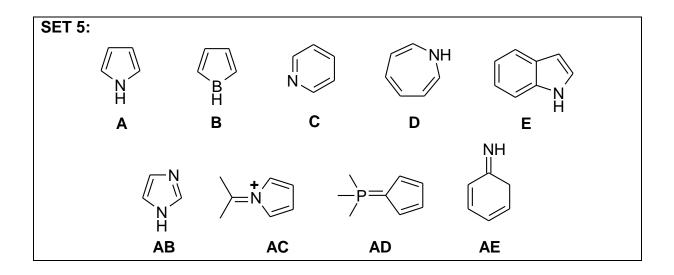
9% PART 3: AROMATICITY AND RESONANCE





Answer questions 22-26 by selecting a <u>single compound</u> from SET 4 above.

- **22**. An aromatic compound where n = 2 in the Huckel rule.
- **23**. A non-aromatic, conjugated triene.
- 24. An anti-aromatic system.
- **25**. A non-conjugated system.
- 26. The neutral compound with the highest resonance energy



Answer questions 27-31 by selecting a <u>single compound</u> from SET 5 above.

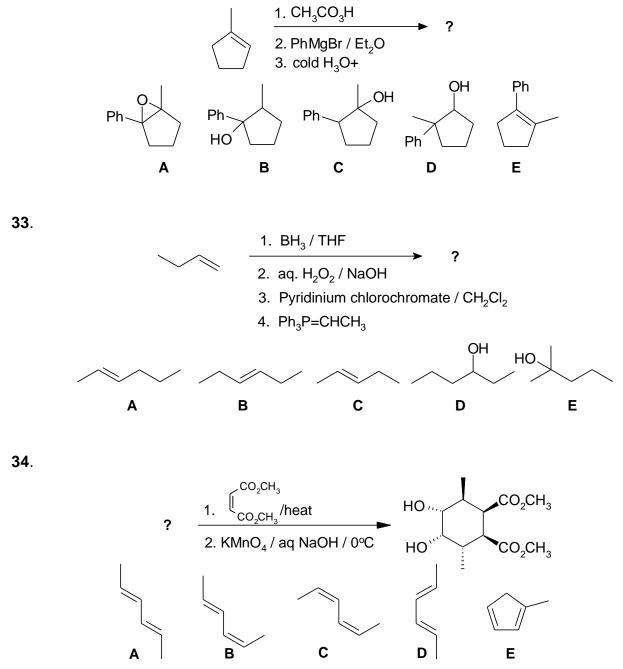
- **27**. An aromatic system that also has an aromatic conjugate acid.
- 28. Non-aromatic as drawn but has an aromatic tautomer.
- **29**. Non-aromatic as drawn but has an important aromatic resonance structure.
- **30**. An anti-aromatic system.
- **31**. An aromatic compound where n = 2 in the Huckel rule.

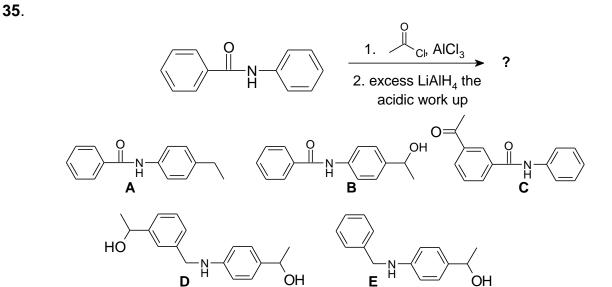
16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 32-40.

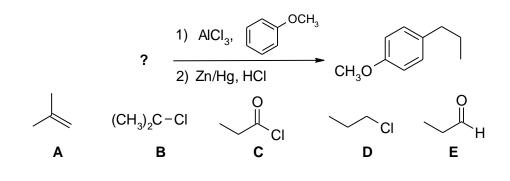
For each of the questions 32 - 40 identify the product(s) obtained or starting material(s) required in order to best complete each of the reaction sequences shown by selecting from the list provided.

32.

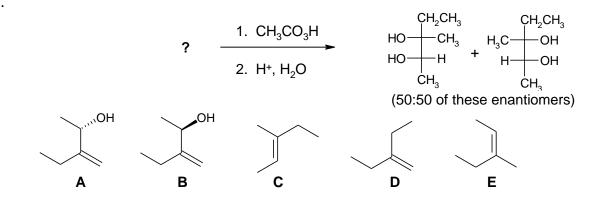




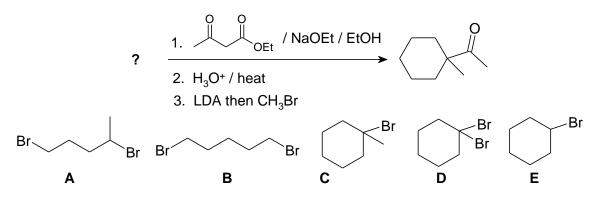
36.



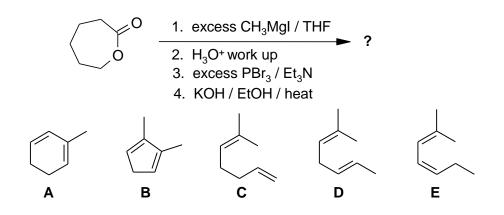
37.



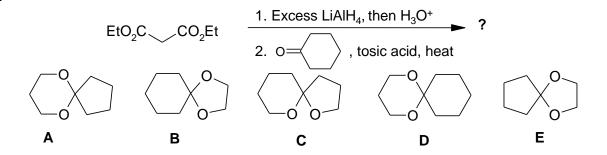
38.



39.



40.

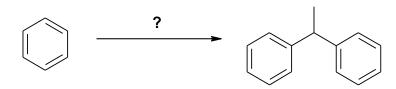


7.5% PART 5: REAGENTS FOR SYNTHESIS

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 41-46

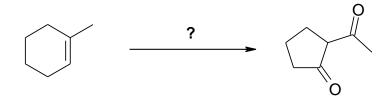
For each of the questions 41-46 identify the reagent sequence required in order to best complete each of the reaction sequences shown.

41.



- **A**. i. Br₂ / FeBr₃ ii. Mg iii. Benzyl bromide
- **B** i. Ethanoyl chloride, AlCl₃ ii. KMnO₄, H₃O⁺, heat iii. benzene
- C. i. Ethyl chloride, AlCl₃ ii. NBS iii. H₂SO₄, heat
- **D**. i. Ethyl chloride, AlCl₃ ii. H_2CrO_4 iii. PhMgBr, then H⁺ workup
- **E**. i. Ethanoyl chloride, AlCl₃ ii. NaBH₄ iii. H⁺, benzene

42.



A. i. HIO₄ ii. OsO₄ / t-butylperoxide / aq. NaOH iii. H₂SO₄, heat

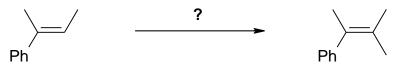
B. i. O_3 ii. Zn iii. LDA, then aqueous workup

C. i. O_3 ii. H_2O_2 iii. MeOH, H⁺ iv. NaOMe, heat

D. i. H_2CrO_4 , heat ii. LiAl H_4 , then H_2O iii. PDC, CH_2Cl_2

E. i. NaNH₂, heat ii. CH₃CO₃H iii aq. H₂SO₄ iv. PCC, CH₂Cl₂

43.



A. i. aq. H₂SO₄ ii. Na metal iii. CH₃I

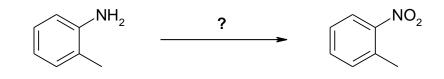
B. i. CH_3CO_3H ii. MeLi then H_2O iii. H_2SO_4 , heat

C. i. KMnO₄, KOH, 0 °C ii. HIO₄ iii. excess MeMgBr then H₂O

D. i. HBr, dark, N₂ ii. MeMgBr iii. aq. H₂SO₄, heat

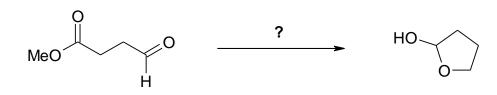
E. i. HBr, peroxides ii. aq. H₂SO₄ iii. Na metal iv. MeBr

44.



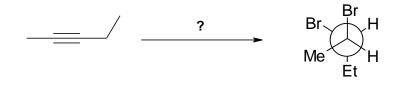
- A. i. KMnO₄, heat ii. NaBH₄
- **B**. i. KMnO₄, heat ii. H₂NNH₂, KOH, heat
- **C**. i. H_2CrO_4 ii. LiAl H_4 iii. H_3O^+ workup
- D. i. KMnO₄, heat ii. NaNO₂, HCl, 0 °C iii HNO₃, H₂SO₄, heat
- E. i. NaNO₂, HCl, 0 °C ii. H₃PO₂ iii. HNO₃, H₂SO₄, heat

45.



- **A**. i. LiAlH₄ then H_2O ii. H_2SO_4 , heat
- **B**. i. 1,3-propane-diol, TsOH ii. LiAlH₄ then H₂O iii. aq. HCl, heat, iv. TsOH, heat
- **C.** i. NaBH₄ ii. 1,2-propane-diol, TsOH iii. LiAlH₄ then H⁺ workup, iv. H₂SO₄, heat
- **D**. i. 1,2-propane-diol, TsOH ii. aq. H₂SO₄, heat iii. TsOH, heat
- E. i. MCPBA ii. aq. HCl, heat iii. Na metal

46.



A. i. H₂, Lindlar's catalyst ii. Br₂, CHCl₃

B. i. Na, liquid NH_3 ii. KMnO₄, KOH, 0 °C iii. excess PBr_3

C. i. Na, liquid NH₃ ii. Br₂, CHCl₃

- **D**. i. H₂, Lindlar's catalyst ii. HBr, peroxides
- E. excess HBr, peroxides

7.5% PART 6: EXPLANATION OF PHENOMENA

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 47 - 52.

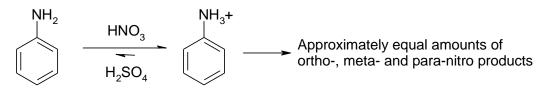
CHOOSE THE <u>SINGLE</u> EXPLANATION THAT <u>BEST</u> RATIONALISES THE PHENOMENON INDICATED.

- **47**. When methyl benzoate is nitrated with HNO₃ / H₂SO₄, the *meta* product is the major product. This is because:
- **A.** The $-NO_2$ group is deactivating and a *meta* director.
- **B.** The $-CO_2CH_3$ group is a *meta* director.
- **C.** The $-OCH_3$ is a *meta* director.
- **D.** Nitration usually occurs at the *meta* position.
- E. Statistically, the *meta* position is preferred over the *para* position.
- **48**. 3,3-dimethylbut-1-ene reacts with aq. H₂SO₄ to give 2,3-dimethylbutan-2-ol because:
- A. Acid catalysed electrophilic addition of water to an alkene follows Markovnikov's rule.
- **B.** Acid catalysed electrophilic addition of water to an alkene is anti-Markovnikov.
- C. The intermediate carbocation undergoes a 1,2-methyl shift.
- **D.** The intermediate carbocation undergoes a 1,2-hydride shift.
- **<u>E.</u>** Water attacks the more substituted end of the system due to the cationic character.
- 49. Pyrrole has a pKa = -3.8 and pyridine has a pKa = 5.2 with respect to their conjugate acids because:

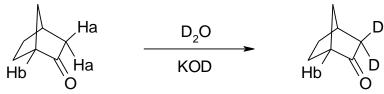
pyrrole
$$\bigvee_{\substack{N \\ H}}$$
 \bigvee_{N} pyridine

- **A.** Pyrrole and pyridine are both aromatic heterocycles where n=1 in the Huckel rule.
- **B.** Pyridine and its conjugate acid are both aromatic heterocycles.
- **C.** Pyrrole and its conjugate acid are both aromatic heterocycles.
- D. Pyridines conjugate acid is aromatic. Pyrroles conjugate acid is non-aromatic.
- **E.** The N atom in pyrrole is sp^2 hybridised.

50. In the nitration of aniline, the first equilibrium is established quickly with majority of starting material as the ammonium salt, shown below. Why is the product not entirely *m*-nitroaniline?



- A. The amino group is a strong activator and directs *meta*.
- **B.** The ammonium group is a strong deactivator and directs *meta*.
- **C.** The nitro group is a strong deactivator and directs *meta*.
- **D.** The rate of reaction of aniline is much faster than protonated aniline.
- E. Steric effects limit the amount of *ortho*-nitro product.
- 51. The bicyclic ketone shown below was reacted in KOD dissolved in D₂O to give only the product shown. Deuterium (D) is a heavier isotope of hydrogen (H).



The H_a protons are more reactive than the H_b protons because:

- **A.** The H_a protons are alpha to a carbonyl.
- **B.** The H_b proton is more acidic.
- **C.** The enolate of H_b is too stable.
- **D.** The bridgehead does not permit enolate formation.
- **E.** Protons H_b and H_a equilibrate by tautomerisation.

52. In general, aldehydes are more reactive towards nucleophiles than ketones because:

- A. Ketones are more electrophilic than aldehydes.
- **B.** The H atom in an aldehyde is an electron withdrawing group.
- C. Alkyl groups are larger than H atoms and are electron donating.
- **D.** Alkyl groups are larger than H atoms and are electron withdrawing.
- E. The reaction is controlled by simple steric effects.

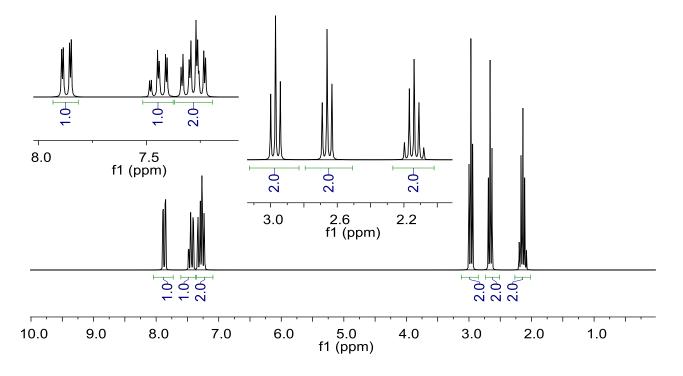
7% PART 7: LABORATORY

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

(3%) Calculate the % yield of propan-1-ol based on the following experimental data:

Borane (20 mL of a 1M solution of borane in THF) in THF (50mL) were stirred at 0 $^{\circ}$ C. Propene (4.2g) was added over 5 min and then the reaction was stirred at room temperature for 2hrs. The reaction was cooled to 0 $^{\circ}$ C and then mixture was treated with an excess of cold alkali hydrogen peroxide, then stirred at 50 $^{\circ}$ C for a further 2hrs then cooled to room temperature. Distillation gave propan-1-ol (3.00g).

(4%) The ¹H NMR spectrum of unknown compound #100 and its functional group test results are shown below. **Draw ONE structure that is consistent with the data**.

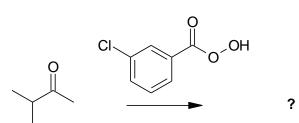


Molecular formula : Solubility test results: Chemical test results: C10H10Oinsoluble in water, aq. acid or aq. base.2,4-D.N.P.: orange precipitateTollen's: no precipitate formedFeCl3: no precipitate formed: no precipitate formed: no precipitate formed

10% PART 8: MECHANISM

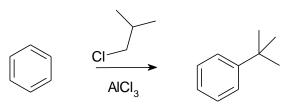
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. ANSWER TWO (2) QUESTIONS, <u>ONE</u> from PART A and <u>ONE</u> from PART B. NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

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



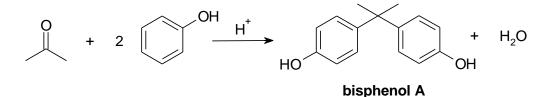
OR ii.

i.



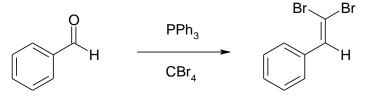
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Provide a detailed mechanism for the formation bisphenol A:



OR

ii. Provide a detailed mechanism showing the steps involved in the following reaction of benzaldehyde with triphenylphosphine and carbon tetrabromide. This reaction is part of the Corey-Fuchs reaction.



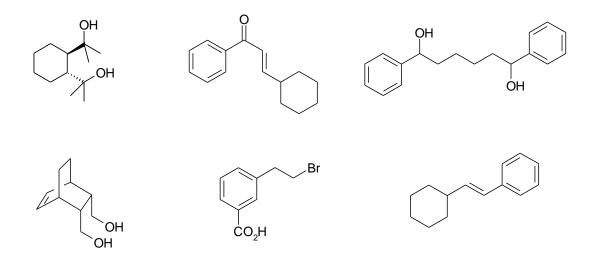
12% PART 9: TOTAL SYNTHESIS

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 FORWARD 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
- cyclohexene

* 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.

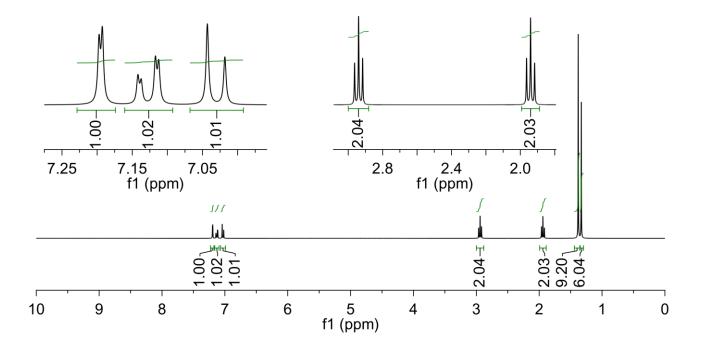
9% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Compound **A**, $C_{11}H_{16}$, was heated with N-chlorosuccinimide or Cl_2 to give **B**, MS M+ = 182, M+2 = 184 (M : M+2 = 3:1). **B** was then slowly added to a solution of diethylmalonate (EtO₂CCH₂CO₂Et) and NaOEt in ethanol to give **C**.

When **C** was then refluxed in aqueous acid, a gas was evolved and compound **D**, $C_{13}H_{18}O_2$ was obtained. Subsequently, **D** was heated with ethanol and an acid catalyst to give **E** IR: absorption at 1735 cm⁻¹, 13C NMR: 173, 151, 138, 128, 127, 61, 34, 33, 31, 30 and 15 ppm.

Reaction of **E** with excess methyl magnesium bromide followed by a normal aqueous acid work up gave **F**, IR: broad absorption at about 3500 cm^{-1} . Reaction of **F** with hot acidic KMnO₄ gave *p*-t-butylbenzoic acid as the major product. Reaction of **F** with conc. H₂SO₄ gave the hydrocarbon **G**, C₁₅H₂₂, as the major product. The H NMR of **G** is shown below:

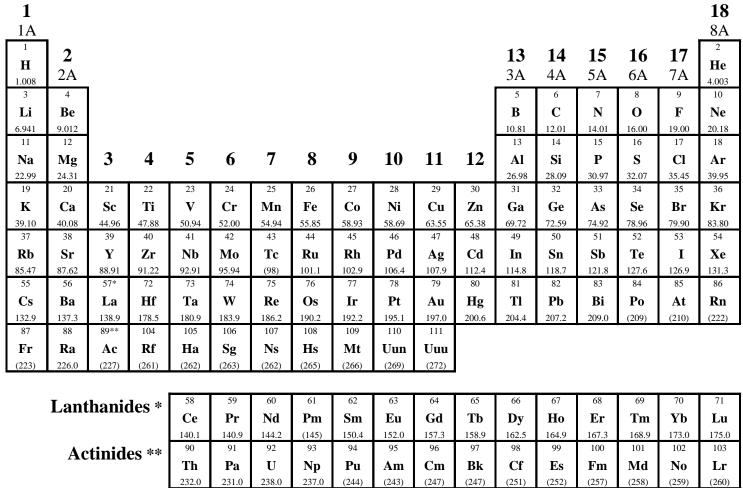


Identify the compounds A, B, C, D, E, F and G (structures are sufficient)

**** THE END ****

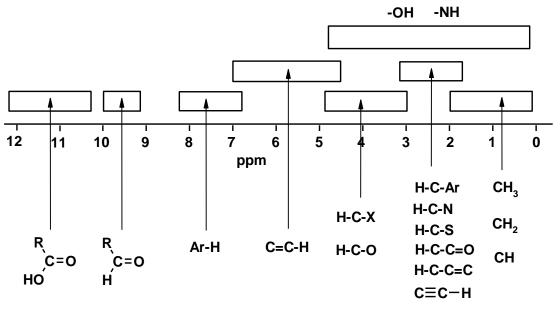
IRH / TS W2011

PERIODIC TABLE



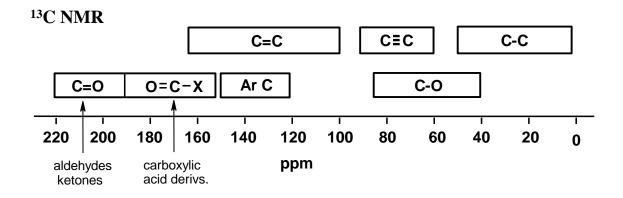
SPECTROSCOPIC TABLES

¹H NMR

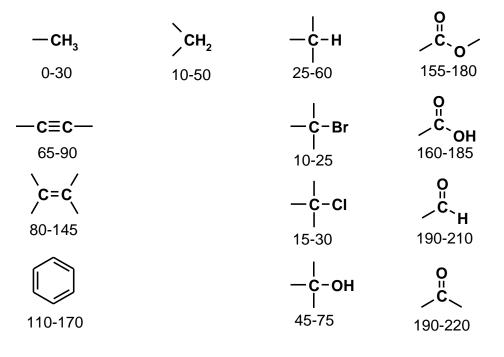


¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	methyl CH ₃ -	methylene -CH ₂ -	methyne CH	other
R−C 	0.9	1.4	1.5	-OH 1-5
R C=C	1.6	2.3	2.6	-NH 1-3 C≡CH 2.5
R R		2.4	2.5	C=C 5.5 Ar-H 7.3
R-N	2.2	2.5	2.9	0 R ^C H ¹⁰
R-Ar	2.3	2.7	3.0	б
R-Br	2.7	3.3	4.1	о с к он ⁹⁻¹²
R-CI	3.1	3.4	4.1	
R-O-	3.3	3.4	3.7	



¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

	<u>T</u>	PE OF VIBRATION	FREQUENCY (cm ⁻¹)	<u>WAVELENGTH</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	1	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, Ether	rs, Esters,			
	Carboxylic acid	ls	1300-1000	7.69-10.0	S
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bondec	I	3400-3200	2.94-3.12	m
	Carboxylic acid	ls (2)	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	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, lodid	е	<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.