# 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 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 $A B$ 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 $>\mathrm{ii}>\mathrm{iii}$ | D | ii $>\mathrm{iii}>\mathrm{i}$ |
| :--- | :--- | :--- | :--- |
| B | $\mathrm{i}>\mathrm{iii}>\mathrm{ii}$ | E | iii $>\mathrm{i}>\mathrm{ii}$ |
| C | $\mathrm{ii}>\mathrm{i}>\mathrm{iii}$ | AB | $\mathrm{iii}>\mathrm{ii}>\mathrm{i}$ |

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

i

ii

iii
2. The relative basicity of the following phenolates:

i

ii

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

i

ii

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

i

ii

iii
5. The relative reactivity toward $\mathrm{Br}_{2} / \mathrm{FeBr}_{3}$ of each of the following:

i

ii

iii

Use the following code to indicate your answers:
A $\quad \mathbf{i}>\mathbf{i i}>\mathbf{i i i}$
D $\quad \mathrm{ii}>\mathrm{iii}>\mathrm{i}$
B $\quad$ i $>\mathrm{iii}>\mathrm{ii}$
E $\quad$ iii $>\mathrm{i}>\mathrm{ii}$
C $\quad$ ii $>$ i $>$ iii
AB $\quad \mathrm{iii}>\mathrm{i}>\mathbf{i}$
6. The relative reactivity of each of the following towards HCl in $\mathrm{CHCl}_{3}$ :

i

ii

iii
7. The relative yield of the para isomer by reacting each of the following with $\mathrm{HNO}_{3}$ / $\mathrm{H}_{2} \mathrm{SO}_{4}$ :

i

ii

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



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

i

ii

iii
10. The relative rate of hydrolysis by $\mathrm{H}_{2} \mathrm{O}$ of each of the following:

i

ii

iii

## 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 $\mathrm{Br}_{2}$.
14. Select ANY TWO structures that are a pair of enantiomers.
SET 2:

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 ${ }^{13} \mathrm{C}$ NMR?

## SET 3



A


B


C


D


E

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 ${ }^{1} \mathrm{H}$-NMR spectrum ?
20. Which compound(s) can be used to acylate benzene using $\mathrm{AlCl}_{3}$ ?
21. Which compound has the most acidic proton?

## 9\% PART 3: AROMATICITY AND RESONANCE

ANSWER NINE (9) OF THE TEN (10) QUESTIONS 22-31.
SET 4:

Answer questions 22-26 by selecting a single compound from SET 4 above.
22. An aromatic compound where $\mathrm{n}=2$ 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

## SET 5:



A


B


C


D


E


AB


AC


AD


AE

Answer questions 27-31 by selecting a single compound 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 $\mathrm{n}=2$ 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.


A

B

C

D

E
33.


34.




C

35.

36.


37.

(50:50 of these enantiomers)

A

B

C

D

E
38.

39.

3. excess $\mathrm{PBr}_{3} / \mathrm{Et}_{3} \mathrm{~N}$
4. $\mathrm{KOH} / \mathrm{EtOH} /$ heat


A


B


C


D


E
40.



A


B


C


D


E

## 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. $\mathrm{Br}_{2} / \mathrm{FeBr}_{3}$ ii. Mg iii. Benzyl bromide

B i. Ethanoyl chloride, $\mathrm{AlCl}_{3}$ ii. $\mathrm{KMnO}_{4}, \mathrm{H}_{3} \mathrm{O}^{+}$, heat iii. benzene
C. i. Ethyl chloride, $\mathrm{AlCl}_{3}$ ii. NBS iii. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat
D. i. Ethyl chloride, $\mathrm{AlCl}_{3}$ ii. $\mathrm{H}_{2} \mathrm{CrO}_{4}$ iii. PhMgBr , then $\mathrm{H}^{+}$workup
E. i. Ethanoyl chloride, $\mathrm{AlCl}_{3}$ ii. $\mathrm{NaBH}_{4}$ iii. $\mathrm{H}^{+}$, benzene
42.



A. i. $\mathrm{HIO}_{4}$ ii. $\mathrm{OsO}_{4} / \mathrm{t}$-butylperoxide / aq. NaOH iii. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat
B. i. $\mathrm{O}_{3}$
ii. Zn
iii. LDA, then aqueous workup
C. i. $\mathrm{O}_{3}$
ii. $\mathrm{H}_{2} \mathrm{O}_{2}$
iii. $\mathrm{MeOH}, \mathrm{H}^{+} \quad$ iv. NaOMe , heat
D. i. $\mathrm{H}_{2} \mathrm{CrO}_{4}$, heat
ii. $\mathrm{LiAlH}_{4}$, then $\mathrm{H}_{2} \mathrm{O}$
iii. $\mathrm{PDC}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$
E. i. $\mathrm{NaNH}_{2}$, heat ii. $\mathrm{CH}_{3} \mathrm{CO}_{3} \mathrm{H}$ iii aq. $\mathrm{H}_{2} \mathrm{SO}_{4}$ iv. $\mathrm{PCC}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$
43.


A. i. aq. $\mathrm{H}_{2} \mathrm{SO}_{4}$ ii. Na metal iii. $\mathrm{CH}_{3} \mathrm{I}$
B. i. $\mathrm{CH}_{3} \mathrm{CO}_{3} \mathrm{H}$ ii. MeLi then $\mathrm{H}_{2} \mathrm{O}$ iii. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat
C. i. $\mathrm{KMnO}_{4}, \mathrm{KOH}, 0^{\circ} \mathrm{C}$ ii. $\mathrm{HIO}_{4}$ iii. excess MeMgBr then $\mathrm{H}_{2} \mathrm{O}$
D. i. HBr , dark, $\mathrm{N}_{2}$ ii. MeMgBr iii. aq. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat
E. i. HBr , peroxides ii. aq. $\mathrm{H}_{2} \mathrm{SO}_{4}$ iii. Na metal iv. MeBr
44.

A. i. $\mathrm{KMnO}_{4}$, heat ii. $\mathrm{NaBH}_{4}$
B. i. $\mathrm{KMnO}_{4}$, heat ii. $\mathrm{H}_{2} \mathrm{NNH}_{2}, \mathrm{KOH}$, heat
C. i. $\mathrm{H}_{2} \mathrm{CrO}_{4}$ ii. $\mathrm{LiAlH}_{4}$ iii. $\mathrm{H}_{3} \mathrm{O}^{+}$workup
D. i. $\mathrm{KMnO}_{4}$, heat ii. $\mathrm{NaNO}_{2}, \mathrm{HCl}, 0^{\circ} \mathrm{C}$ iii $\mathrm{HNO}_{3}, \mathrm{H}_{2} \mathrm{SO}_{4}$, heat
E. i. $\mathrm{NaNO}_{2}, \mathrm{HCl}, 0^{\circ} \mathrm{C}$ ii. $\mathrm{H}_{3} \mathrm{PO}_{2}$ iii. $\mathrm{HNO}_{3}, \mathrm{H}_{2} \mathrm{SO}_{4}$, heat
45.

A. i. $\mathrm{LiAlH}_{4}$ then $\mathrm{H}_{2} \mathrm{O}$ ii. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat
B. i. 1,3-propane-diol, TsOH ii. $\mathrm{LiAlH}_{4}$ then $\mathrm{H}_{2} \mathrm{O}$ iii. aq. HCl , heat, iv. TsOH , heat
C. i. $\mathrm{NaBH}_{4}$ ii. 1,2-propane-diol, TsOH iii. $\mathrm{LiAlH}_{4}$ then $\mathrm{H}^{+}$workup, iv. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat
D. i. 1,2-propane-diol, TsOH ii. aq. $\mathrm{H}_{2} \mathrm{SO}_{4}$, heat iii. TsOH , heat
E. i. MCPBA ii. aq. HCl , heat iii. Na metal
46.

A. i. $\mathrm{H}_{2}$, Lindlar's catalyst ii. $\mathrm{Br}_{2}, \mathrm{CHCl}_{3}$
B. i. Na , liquid $\mathrm{NH}_{3} \quad$ ii. $\mathrm{KMnO}_{4}, \mathrm{KOH}, 0^{\circ} \mathrm{C}$ iii. excess $\mathrm{PBr}_{3}$
C. i. Na , liquid $\mathrm{NH}_{3}$
ii. $\mathrm{Br}_{2}, \mathrm{CHCl}_{3}$
D. i. $\mathrm{H}_{2}$, 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 SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

47. When methyl benzoate is nitrated with $\mathrm{HNO}_{3} / \mathrm{H}_{2} \mathrm{SO}_{4}$, the meta product is the major product. This is because:
A. The $-\mathrm{NO}_{2}$ group is deactivating and a meta director.
B. The $-\mathrm{CO}_{2} \mathrm{CH}_{3}$ group is a meta director.
C. The $-\mathrm{OCH}_{3}$ 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. $\mathrm{H}_{2} \mathrm{SO}_{4}$ 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.
E. Water attacks the more substituted end of the system due to the cationic character.
49. Pyrrole has a $\mathrm{pKa}=-3.8$ and pyridine has a $\mathrm{pKa}=5.2$ with respect to their conjugate acids because:

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 $\mathrm{sp}^{2}$ 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 $\mathrm{D}_{2} \mathrm{O}$ to give only the product shown. Deuterium (D) is a heavier isotope of hydrogen (H).




The $\mathrm{H}_{\mathrm{a}}$ protons are more reactive than the $\mathrm{H}_{\mathrm{b}}$ protons because:
A. The $\mathrm{H}_{\mathrm{a}}$ protons are alpha to a carbonyl.
B. The $\mathrm{H}_{\mathrm{b}}$ proton is more acidic.
C. The enolate of $\mathrm{H}_{\mathrm{b}}$ is too stable.
D. The bridgehead does not permit enolate formation.
E. Protons $\mathrm{H}_{\mathrm{b}}$ and $\mathrm{H}_{\mathrm{a}}$ 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 1 M solution of borane in THF) in THF ( 50 mL ) were stirred at $0^{\circ} \mathrm{C}$. Propene ( 4.2 g ) was added over 5 min and then the reaction was stirred at room temperature for 2 hrs . The reaction was cooled to $0^{\circ} \mathrm{C}$ and then mixture was treated with an excess of cold alkali hydrogen peroxide, then stirred at $50^{\circ} \mathrm{C}$ for a further 2 hrs then cooled to room temperature. Distillation gave propan-1-ol (3.00g).
(4\%) The ${ }^{1} \mathrm{H}$ 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 : $\quad \mathrm{C}_{10} \mathrm{H}_{10} \mathrm{O}$
Solubility test results: insoluble in water, aq. acid or aq. base.
Chemical test results: 2,4-D.N.P. : orange precipitate
Tollen's : no precipitate formed
$\mathrm{FeCl}_{3} \quad$ : no colour change
$\mathbf{I}_{2} / \mathbf{K O H}$ : no precipitate formed

## 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 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 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 $\mathbf{A}, \mathrm{C}_{11} \mathrm{H}_{16}$, was heated with N -chlorosuccinimide or $\mathrm{Cl}_{2}$ to give $\mathrm{B}, \mathrm{MS} \mathrm{M}+=182$, $\mathrm{M}+2=184 \quad(\mathrm{M}: \mathrm{M}+2=3: 1)$. $\quad \mathrm{B}$ was then slowly added to a solution of diethylmalonate $\left(\mathrm{EtO}_{2} \mathrm{CCH}_{2} \mathrm{CO}_{2} \mathrm{Et}\right)$ and NaOEt in ethanol to give $\mathbf{C}$.
When $\mathbf{C}$ was then refluxed in aqueous acid, a gas was evolved and compound D, $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{O}_{2}$ was obtained. Subsequently, D was heated with ethanol and an acid catalyst to give E IR: absorption at $1735 \mathrm{~cm}^{-1}, 13 C$ NMR: 173, 151, 138, 128, 127, 61, 34, 33, 31, 30 and 15 ppm .
Reaction of $\mathbf{E}$ with excess methyl magnesium bromide followed by a normal aqueous acid work up gave $\mathbf{F}$, IR: broad absorption at about $3500 \mathrm{~cm}^{-1}$. Reaction of $\mathbf{F}$ with hot acidic $\mathrm{KMnO}_{4}$ gave $p$-t-butylbenzoic acid as the major product. Reaction of $\mathbf{F}$ with conc. $\mathrm{H}_{2} \mathrm{SO}_{4}$ gave the hydrocarbon $\mathbf{G}, \mathrm{C}_{15} \mathrm{H}_{22}$, as the major product. The H NMR of $\mathbf{G}$ is shown below:


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

## PERIODIC TABLE



| Lanthanides * | $\begin{gathered} 58 \\ \mathbf{C e} \\ 140.1 \\ \hline \end{gathered}$ | $\begin{gathered} 59 \\ \mathbf{P r} \\ 140.9 \end{gathered}$ | 60 <br> Nd <br> 144.2 | 61 <br> Pm <br> (145) | $\begin{gathered} 62 \\ \mathbf{S m} \\ 150.4 \end{gathered}$ | $\begin{gathered} 63 \\ \mathbf{E u} \\ 152.0 \end{gathered}$ | 64 <br> Gd <br> 157.3 | $\begin{gathered} 65 \\ \mathbf{T b} \\ 158.9 \\ \hline \end{gathered}$ | 66 Dy $162.5$ | 67 <br> Но <br> 164.9 | $\begin{gathered} 68 \\ \text { Er } \\ 167.3 \end{gathered}$ | $\begin{gathered} 69 \\ \mathbf{T m} \\ 168.9 \end{gathered}$ | $\begin{gathered} 70 \\ \mathbf{Y b} \\ 173.0 \end{gathered}$ | $\begin{gathered} 71 \\ \mathbf{L u} \\ 175.0 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Actinides ** | $\begin{gathered} \hline 90 \\ \mathbf{T h} \\ 232.0 \end{gathered}$ | $\begin{gathered} 91 \\ \mathbf{P a} \\ 231.0 \end{gathered}$ | $\begin{gathered} 92 \\ \mathbf{U} \\ 238.0 \end{gathered}$ | $93$ <br> Np $237.0$ | 94 <br> $\mathbf{P u}$ <br> (244) | $\begin{gathered} 95 \\ \text { Am } \\ (243) \end{gathered}$ | $\begin{gathered} \hline 96 \\ \mathrm{Cm} \end{gathered}$ | 97 <br> Bk <br> (247) | $\begin{gathered} 98 \\ \text { Cf } \\ (251) \end{gathered}$ | 99 <br> Es <br> (252) | $\begin{gathered} 100 \\ \text { Fm } \\ (257) \end{gathered}$ | $\begin{gathered} 101 \\ \mathbf{M d} \\ (258) \end{gathered}$ | $\begin{gathered} 102 \\ \text { No } \\ (259) \\ \hline \end{gathered}$ | $\begin{gathered} 103 \\ \mathbf{L r} \\ (260) \end{gathered}$ |

${ }^{1} \mathrm{H}$ NMR

${ }^{1}$ H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

|  | methyl $\mathrm{CH}_{3}-$ | methylene $-\mathrm{CH}_{2}-$ | methyne CH | other |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0.9 | 1.4 | 1.5 | $-\mathrm{OH}$ | 1-5 |
|  |  |  |  | -NH | 1-3 |
| ${ }_{\prime}^{R_{1}}=c^{\prime}$ | 1.6 | 2.3 | 2.6 | $\mathrm{C} \equiv \mathrm{CH}$ | 2.5 |
| O | 2.1 | 2.4 | 2.5 | $\mathrm{C}=\mathrm{C}$ | 5.5 |
|  |  |  |  | Ar-H | 7.3 |
| $R-N^{\prime}$ | 2.2 | 2.5 | 2.9 |  | 10 |
| R-Ar | 2.3 | 2.7 | 3.0 | O |  |
| $\mathrm{R}-\mathrm{Br}$ | 2.7 | 3.3 | 4.1 |  | 9-12 |
| R-Cl | 3.1 | 3.4 | 4.1 |  |  |
| R-O- | 3.3 | 3.4 | 3.7 |  |  |

${ }^{13}$ C NMR

${ }^{13} \mathrm{C}$ NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

| $\begin{gathered} -\mathrm{CH}_{3} \\ 0-30 \end{gathered}$ | $\xrightarrow[\substack{ \\10-50}]{\mathrm{CH}_{2}}$ |  |  |
| :---: | :---: | :---: | :---: |
| $\begin{gathered} \text { — } \equiv \mathbf{C}- \\ 65-90 \end{gathered}$ |  |  |  |
|  |  |  |  |
| 110-170 |  |  |  |

## INFRA-RED GROUP ABSORPTION FREQUENCIES

| C-H | TYPE OF VIBRATION | FREQUENCY $\left(\mathrm{cm}^{-1}\right)$ | WAVELENGTH $(\mu)$ | INTENSITY (1) |
| :---: | :---: | :---: | :---: | :---: |
|  | Alkanes (stretch) | 3000-2850 | 3.33-3.51 | S |
|  | $-\mathrm{CH}_{3}$ (bend) | 1450 and 1375 | 6.90 and 7.27 | m |
|  | $-\mathrm{CH}_{2}{ }^{-}$(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 |  |  |  |
| $\mathrm{C}=\mathrm{C}$ | Alkene | 1680-1600 | 5.95-6.25 | m-w |
|  | Aromatic | 1600-1400 | 6.25-7.14 | m-w |
| $\mathrm{C} \equiv \mathrm{C}$ | Alkyne | 2250-2100 | 4.44-4.76 | m-w |
| $\mathrm{C}=\mathrm{O}$ | 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-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 (2) | 3300-2500 | 3.03-4.00 | m |
| $\mathrm{N}-\mathrm{H}$ | Primary and secondary amines | ca. 3500 | ca. 2.86 | m |
| $\mathrm{C} \equiv \mathrm{N}$ | Nitriles | 2260-2240 | 4.42-4.46 | m |
| $\mathrm{N}=\mathrm{O}$ | Nitro (R-NO2) | 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, 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.

