

Please check whether you have got the right question paper.

N.B:(1) **All** questions are **compulsory**

(2) **Figures** to the **right** indicate **full** marks

(3) Answer **all** the sub-questions **together** and in **order**

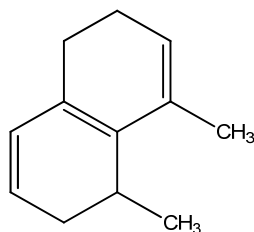
(4) **Spectral** correlation **tables** are **allowed**

**Q.1 (a) Answer any four questions (1 mark each) (4)**

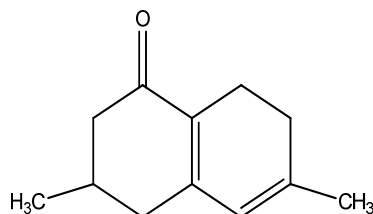
- (i) Predict the number of signals in the  $^{13}\text{C}$  NMR spectrum of *o* dichlorobenzene
- (ii) Predict the number of signals in the  $^1\text{H}$  NMR spectrum of hexan-3-one
- (iii) Draw structure of the ion responsible for the base peak in mass spectrum of *n* propanol
- (iv) Calculate the index of hydrogen deficiency for  $\text{C}_8\text{H}_7\text{N}$
- (v) Give the coupling constant value for *cis* coupled protons for substituted alkene
- (vi) Arrange the following in increasing order of frequency for C=O stretch  
Aliphatic ketones,  $\alpha\beta$  unsaturated ketone,  $\alpha\beta$  unsaturated amide

**(b) Answer any eight questions (2 Marks each) (16)**

(i) Predict UV  $\lambda_{\text{max}}$  of



(ii) Predict UV  $\lambda_{\text{max}}$  of

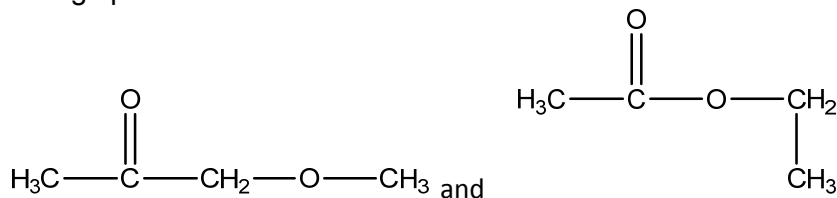


(iii) How will you distinguish between the following by  $^1\text{H}$  NMR spectroscopy? Give distinguishing spectral data

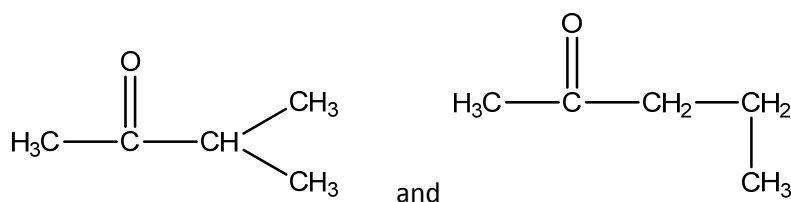


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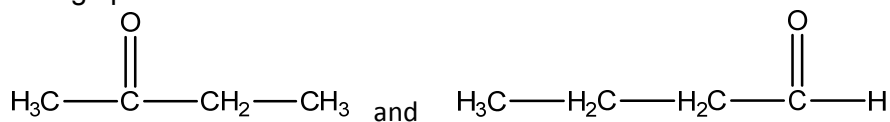
(iv) How will you distinguish between the following compounds by IR spectroscopy? Give distinguishing spectral data



(v) How will you distinguish between the following by mass spectrometry? Give distinguishing spectral data

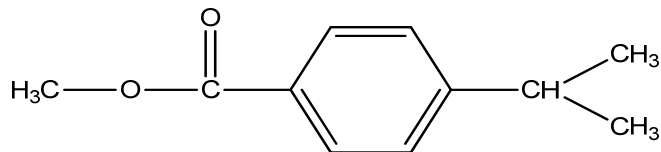


(vi) How will you distinguish between the following by  $^{13}\text{C}$  NMR spectroscopy? Give distinguishing spectral data



(vii) Depict one fragmentation pathway for 1-methylcyclohexene?

(viii) Predict  $^1\text{H}$  NMR spectrum of the following giving  $\delta$  value, splitting pattern and ratio of proton intensity. Do not give ranges.



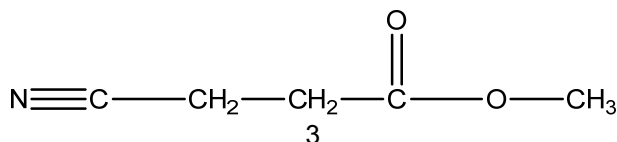
(ix) A compound with molecular formula  $\text{C}_4\text{H}_6\text{O}_4$  gives only two  $^{13}\text{C}$  NMR signals while  $^1\text{H}$  NMR shows only one 2 signals, at and  $\delta 2.2$ . Deduce the structure and justify your answer

(x) Predict the IR spectrum of aniline.

**Q.2 Answer any five questions (5x7 marks)**

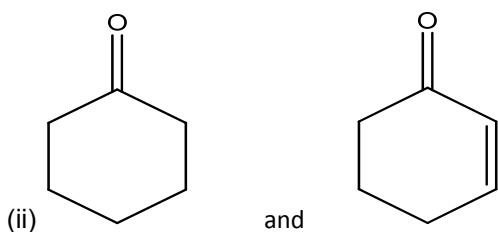
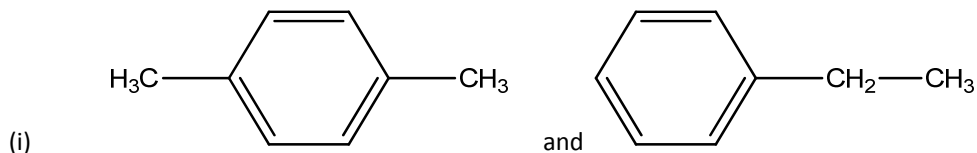
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a Predict IR spectrum,  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectrum of



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- b How will you distinguish between following compounds using spectral techniques? Give distinguishing spectral characteristics. If mass spectrometry is used, one fragmentation pathway must be depicted



Write all possible structures for compound with molecular formula  $C_4H_8O$  and whose IR spectrum shows a band at around  $1720\text{ cm}^{-1}$ . Predict  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR of each structure.

- c A compound with molecular weight 134 has a prominent band at  $1693\text{ cm}^{-1}$  in its IR spectrum. The  $^1\text{H}$  NMR spectrum shows two singlets in the ratio of 2:1 at  $\delta 8$  and  $\delta 10$ .  $^{13}\text{C}$  NMR spectrum gives 3 signals at  $\delta 130$ (d), 139(s) and 191 (d). Mass spectrum shows  $m/z$  134, 133, 105, 77, 51 and 29. Predict the structure and justify your answer. Depict how fragments 133 and 29 are formed.

A compound with molecular weight 156 shows IR bands at 3060, 2935, 2200 and  $1600\text{ cm}^{-1}$ .

The  $^1\text{H}$  NMR spectrum shows the following spectral characteristics

$\delta 7.3$  s 4H

$\delta 2.6$  s 4H

- e The  $^{13}\text{C}$  NMR spectrum shows the following signals  
 $\delta 168$  s, 136 s, 125 d, 30 t.

Deduce the structure and justify your answer.

A compound with molecular formula  $C_{10}H_{12}O_3$  has a prominent band at  $1742\text{ cm}^{-1}$  in its IR spectrum.

The  $^1\text{H}$  NMR spectrum shows the following spectral characteristics

$\delta 7.9$  dd 2H

$\delta 6.9$  dd 2H

$\delta 4.0$  q 2H

$\delta 3.8$  s 3H

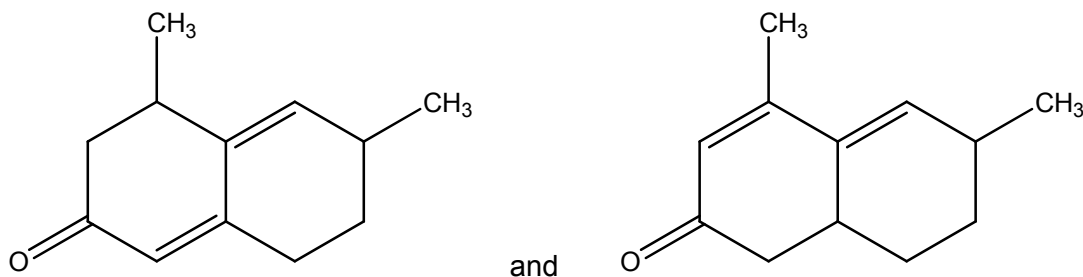
$\delta 1.4$  t 3H

- f Predict the structure and justify your answer

- g Predict the  $^1\text{H}$  NMR and mass spectrum of *p* methoxyisopropyl benzene. Depict two fragmentation pathways for the molecule, one involving fission and the other rearrangement

**3 Answer any 5 questions (5x4 marks)**

- a Distinguish between the following using a suitable spectral technique



- b Draw all possible structural isomers of  $\text{C}_3\text{H}_6\text{O}$ . Predict the number of signals in  $^{13}\text{C}$  NMR of each isomer
- c A compound with molecular formula  $\text{C}_4\text{H}_8\text{O}_2$  has an IR band at 1150, a  $^1\text{H}$  NMR singlet at  $\delta$  3.95 and one signal at  $\delta$  66.5 in its  $^{13}\text{C}$  NMR spectrum. Predict its structure and justify your answer.
- d A compound has  $m/z$  values of 112, 114 and 116 in the molecular ion region of the mass spectrum. The  $^1\text{H}$  NMR spectrum has two doublets of equal intensity at  $\delta$  4.1 and 9.2. Deduce the structure and justify your answer.
- e A compound with molecular weight 123 has following spectral characteristics  
 $^1\text{H}$  NMR:  $\delta$  8.1 (2H, m), 7.5 (3H, m) and it shows IR bands at 3030, 1600, 1550, 1500  $\text{cm}^{-1}$ .  
 Deduce its structure and justify your answer.
- f Predict the IR and  $^{13}\text{C}$  NMR spectra for *p*-nitrobenzaldehyde
- g Depict two fragmentation pathways for pentan-2-one, one involving fission and the other involving rearrangement

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## SPECTRAL CORRELATION TABLES

Chemical Shifts for Methylene Groups Attached to Two Functional Groups (Y—CH<sub>2</sub>—Z)

GROUP	-CH <sub>3</sub>	-C≡C	-O-C	-Ph	-CF <sub>3</sub>	-CF <sub>2</sub>	-Cl	-Br	-I	-OH	-OR	-OPh	-OC(=O)R	-C(=O)R	-C(=O)Ph	-C(=O)OR	-C(=O)NR <sub>2</sub>	-CON	-NR <sub>2</sub>	-NHC(=O)R	-N <sub>3</sub>	-SR
-CH <sub>3</sub>	1.17	1.90	2.14	2.55	1.91	1.84	3.57	3.43	3.20	3.70	3.40	4.25	2.47	2.25	2.23	2.25	2.29	2.40	2.27	2.97	2.67	2.53
-C≡C	2.60	3.39	3.30				3.23	3.03	2.52	3.26	3.06	3.93	3.83	2.40	2.54	2.25	2.29	2.40	2.27	2.97	2.67	2.34
-O-C	2.87	2.99	3.40	2.76	2.69	4.08	3.88	3.37	4.13	3.91	4.78	4.68	3.25	3.39	3.10	3.14	3.25	3.12	3.82	3.52	3.19	
-Ph	3.11	3.52	2.88	2.81	4.09	3.90	4.20	4.00	3.49	4.28	4.03	4.90	4.71	3.37	3.51	3.22	3.26	3.37	3.24	3.97	3.67	3.31
-CF <sub>3</sub>	3.87	3.50	4.50	4.35			4.20	4.00	3.49	4.28	4.03	4.90	4.71	3.37	3.51	3.22	3.26	3.37	3.24	3.97	3.67	3.31
-CF <sub>2</sub>	3.93	3.29	3.22	4.61	4.41	3.90	4.58	4.44	5.31	5.21	3.78	3.92	3.63	3.66	3.78	3.65	3.48	4.34	4.04	3.72		
-Cl	2.63	2.58	3.97	3.76	3.26	4.01				4.01	3.80	4.67	4.57	3.12	3.28	2.99	3.03	3.12	3.01	3.71	3.41	3.08
-Br	2.51	3.90	3.70	3.19	3.93	4.73	4.60	4.54	3.07	3.21	2.92	2.96	3.07	2.94	3.64	3.34	3.01					
-I	4.99	5.16	4.99	5.40																		
-OH	5.29	5.09	4.58	5.32	5.12	5.99	5.89	4.46	4.60	4.31	4.35	4.46	4.31	4.35	4.46	4.37	5.13	4.73	4.40			
-OR	4.94	4.89	4.38	5.12	4.92	5.79	5.69	4.26	3.40	4.11	4.15	4.26	4.13	4.26	4.13	4.15	4.26	4.13	4.83	4.53	4.20	
-OPh	3.90	3.87	4.61	4.41	5.16	5.06	3.75	3.89	3.60	3.64	3.75	3.62	4.32	4.02	3.69							
-OC(=O)R	4.55	4.35	5.15	6.03	5.92	4.49	4.63	4.34	4.38	4.49	4.33	5.06	4.78	4.43								
-C(=O)R	4.55	4.35	5.15	6.03	5.92	4.49	4.63	4.34	4.38	4.49	4.33	5.06	4.78	4.43								
-C(=O)Ph	4.95	5.82	5.72	4.29	4.43	4.22	4.18	4.29	4.15	4.94	4.64	4.23										
-C(=O)OR	6.69	6.59	5.16	5.30	5.09	4.05	5.16	5.03	5.86	5.56	5.10											
-C(=O)NR <sub>2</sub>	6.46	5.10	5.20	4.91	4.95	5.10	4.92	5.63	5.37	5.00												
-CON	3.60	3.63	3.77	3.48	3.52	3.63	3.50	4.20	3.90	3.57												
-NR <sub>2</sub>	3.91	3.62	3.66	3.77	3.64	4.34	4.02	3.71														
-NHC(=O)R	3.35	3.33	3.37	3.48	3.35	4.05	3.75	3.42														
-N <sub>3</sub>	3.30	3.41	3.52	3.39	4.09	3.79	3.46															
-SR	3.63	3.50	4.20	3.90	3.57																	

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## CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

Group	Range $\mu$	Intensity	Range $\text{cm}^{-1}$	Intensity
<b>A. Hydrocarbon chromophore</b>				
<b>1. C-H STRETCHING</b>				
a. Alkane	3.38-3.51	(m-s)	2952-2853	(m)
b. Alkene, monosubstituted (viny)	3.29-3.32	(m)	3040-3010	(m)
	and 3.23-3.25	(m)	3095-3075	(m)
Alkene, disubstituted, <i>cis</i>	3.29-3.32	(m)	3040-3010	(m)
Alkene, disubstituted, <i>trans</i>	3.29-3.32	(m)	3040-3010	(m)
Alkene, disubstituted, <i>gem</i>	3.23-3.25	(m)	3095-3075	(m)
Alkene, trisubstituted	3.29-3.32	(m)	3040-3010	(m)
c. Alkyne	~3.03	(s)	~3300	(s)
d. Aromatic	~3.30	(v)	~3000	(v)
<b>2. C-H BENDING</b>				
a. Alkane, C-H	~7.46	(w)	~1340	(w)
Alkane, -CH <sub>2</sub>	6.74-6.92	(m)	1465-1445	(m)
Alkane, -CH <sub>3</sub>	6.80-7.00	(m)	1470-1430	(m)
Alkane, <i>gem</i> -dimethyl	7.25-7.30	(s)	1385-1370	(s)
	7.22-7.25	(s)	1385-1380	(s)
	and 7.30-7.33	(s)	1370-1365	(s)
Alkane, <i>tert</i> -butyl	7.17-7.22	(m)	1385-1385	(m)
	and ~7.33	(s)	~1365	(s)
b. Alkene, monosubstituted (viny)	10.05-10.15	(s)	995-985	(s)
	10.93-11.05	(s)	915-905	(s)
	and 7.04-7.09	(s)	1430-1410	(s)
	and ~14.57	(s)	~690	(s)
	10.31-10.42	(s)	970-960	(s)
	and 7.64-7.72	(m)	1370-1295	(m)
Alkene, disubstituted, <i>cis</i>	11.17-11.30	(s)	895-885	(s)
Alkene, disubstituted, <i>trans</i>	7.04-7.09	(s)	1420-1410	(s)
	11.90-12.66	(s)	800-790	(s)
	~15.9	(s)	~630	(s)
c. Alkyne	~13.3	(v, s)	~750	(v, s)
	and ~14.3	(v, s)	~700	(v, s)
	~13.3	(v, s)	~750	(v, s)
	~12.8	(v, m)	~780	(v, m)
	~12.0	(v, m)	~830	(v, m)
	~11.3	(v, w)	~880	(v, w)
<b>3. C-C MULTIPLE BOND STRETCHING</b>	5.95-6.17	(v)	1680-1620	(v)
a. Alkene, nonconjugated	~6.08	(m)	~1645	(m)
Alkene, monosubstituted (viny)	~6.03	(m)	~1638	(m)
Alkene, disubstituted, <i>cis</i>	~5.97	(m)	~1675	(m)
Alkene, disubstituted, <i>trans</i>				
<b>B. Carbonyl chromophore</b>				
<b>1. KETONE STRETCHING VIBRATIONS</b>				
a. Saturated, acyclic	5.80-5.87	(s)	1725-1705	(s)
b. Saturated, cyclic:				
6-membered ring (and higher)	5.80-5.87	(s)	1725-1705	(s)
5-membered ring	5.71-5.75	(s)	1750-1740	(s)
4-membered ring	~5.67	(s)	~1775	(s)
c. $\alpha,\beta$ -Unsaturated, acyclic	5.94-6.01	(s)	1685-1665	(s)
d. $\alpha,\beta$ -Unsaturated, cyclic:				
6-membered ring (and higher)	5.90-6.04	(s)	1685-1665	(s)
5-membered ring	5.80-5.85	(s)	1725-1708	(s)
4-membered ring	5.99-6.01	(s)	1670-1663	(s)
e. $\alpha,\beta$ -Unsaturated, acyclic	5.88-5.95	(s)	1700-1680	(s)
f. Aryl	5.99-6.02	(s)	1670-1660	(s)
g. Diaryl	5.78-5.83	(s)	1730-1710	(s)
h. $\alpha$ -Diketones	6.10-6.50	(s)	1640-1540	(s)
i. $\beta$ -Diketones (enolic)	5.92-6.02	(s)	1690-1660	(s)
j. 1,4-Quinones	~4.65	(s)	~2150	(s)
k. Ketenes				
<b>2. ALDEHYDES</b>				
a. Carbonyl stretching vibrations				
Saturated, aliphatic	5.75-5.81	(s)	1740-1720	(s)
$\alpha,\beta$ -Unsaturated, aliphatic	5.87-5.95	(s)	1705-1680	(s)
$\alpha,\beta,\gamma,\delta$ -Unsaturated, aliphatic	5.95-6.02	(s)	1680-1650	(s)
Aryl	5.83-5.90	(s)	1715-1695	(s)
b. C-H stretching vibrations, two bands	3.45-3.55	(w)	2900-2820	(w)
and 3.60-3.70			2775-2700	
<b>3. ESTER STRETCHING VIBRATIONS</b>				
a. Saturated, acyclic	5.71-5.76	(s)	1750-1735	(s)
b. Saturated, cyclic:				
$\delta$ -lactones (and larger rings)	5.73-5.76	(s)	1750-1735	(s)
$\gamma$ -lactones	5.83-5.88	(s)	1780-1760	(s)
$\beta$ -lactones	~5.81	(s)	~1820	(s)

Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp.  
 ~ = approximately

## CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

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Group	Range, $\mu$	Intensity	Range $\text{cm}^{-1}$
c. Unsaturated:			
vinyl ester type	5.56-5.65	(s)	1800-1770
$\alpha,\beta$ -unsaturated and aryl	5.78-5.82	(s)	1730-1717
$\alpha,\beta$ -unsaturated $\beta$ -lactone	5.78-5.82	(s)	1730-1717
$\alpha,\beta$ -unsaturated $\gamma$ -lactone	5.68-5.75	(s)	1760-1740
$\beta,\gamma$ -unsaturated $\gamma$ -lactone	~5.56	(s)	~1800
d. $\alpha$ -Ketoesters	5.70-5.75	(s)	1755-1740
e. $\beta$ -Ketoesters (enolic)	~6.06	(s)	~1650
f. Carbonates	5.62-5.75	(s)	1786-1740
CARBOXYLIC ACIDS			
a. Carbonyl stretching vibrations: saturated aliphatic	5.80-5.88	(s)	1725-1700
$\alpha,\beta$ -unsaturated aliphatic	5.83-5.92	(s)	1715-1690
aryl	5.88-5.95	(s)	1700-1680
b. Hydroxyl stretching (bonded): several bands	3.70-4.00	(w)	2700-2500
c. Carboxylate anion stretching	6.21-6.45	(s)	1610-1550
and	7.15-7.69	(s)	1400-1300
ANHTRIDE STRETCHING VIBRATIONS			
a. Saturated, acyclic	5.41-5.56	(s)	1850-1800
and	5.59-5.75	(s)	1790-1740
b. $\alpha,\beta$ -Unsaturated and aryl, acyclic	5.47-5.62	(s)	1830-1780
and	5.65-5.81	(s)	1770-1720
c. Saturated, 5-membered ring	5.35-5.49	(s)	1870-1820
and	5.56-5.71	(s)	1800-1750
d. $\alpha,\beta$ -Unsaturated, 5-membered ring	5.41-5.56	(s)	1850-1800
and	5.47-5.62	(s)	1830-1780
ACYL HALIDE STRETCHING VIBRATIONS			
a. Acyl fluorides	~5.41	(s)	~1850
b. Acyl chlorides	~5.57	(s)	~1795
c. Acyl bromides	~5.53	(s)	~1810
d. $\alpha,\beta$ -Unsaturated and aryl	5.61-5.72	(s)	1780-1750
and	5.72-5.82	(m)	1750-1720
e. $\text{COF}_2$	5.19	(s)	1928
f. $\text{COCl}_2$	5.47	(s)	1828
g. $\text{COBr}_2$	5.47	(s)	1828
7. AMIDES			
a. Carbonyl stretching vibrations			
Primary, solid and concentrated solution	~6.06	(s)	~1650
Primary, dilute solution	~5.92	(s)	~1690
Secondary, solid and concentrated solution	5.95-6.14	(s)	1680-1630
Secondary, dilute solution	5.88-5.99	(s)	1700-1670
Tertiary, solid and all solutions	5.99-6.14	(s)	1670-1630
Cyclic, $\beta$ -lactams, dilute solution	~5.95	(s)	~1680
Cyclic, $\gamma$ -lactams, dilute solution	~5.88	(s)	~1700
Group	Range, $\mu$	Intensity	Range $\text{cm}^{-1}$
Cyclic, $\gamma$ -lactams, fused to another ring, dilute solution	5.71-5.88	(s)	1750-1700
Cyclic, $\beta$ -lactams, dilute solution	5.68-5.78	(s)	1760-1730
Cyclic, $\beta$ -lactams, fused to another ring, dilute solution	5.62-5.65	(s)	1780-1770
Ureas, acyclic	~6.02	(s)	~1660
Ureas, cyclic, 6-membered ring	~6.10	(s)	~1640
Ureas, cyclic, 5-membered ring	~5.81	(s)	~1720
Urethanes	5.75-5.92	(s)	1740-1690
Imides, acyclic	~5.85	(s)	~1710
and	~5.88	(s)	~1700
Imides, cyclic, 6-membered ring	~5.85	(s)	~1710
and	~5.88	(s)	~1700
Imides, cyclic, $\alpha,\beta$ -unsaturated, 6-membered ring	~5.78	(s)	~1730
and	~5.99	(s)	~1670
Imides, cyclic, 5-membered ring	~5.65	(s)	~1770
and	~5.88	(s)	~1700
Imides, cyclic, $\alpha,\beta$ -unsaturated, 5-membered ring	~5.59	(s)	~1790
and	~5.85	(s)	~1710
b. N—H Stretching vibrations			
Primary, free: two bands	~2.86	(m)	~3500
and	~2.94	(m)	~3400
Primary, bonded: two bands	~2.99	(m)	~3350
and	~3.15	(m)	~3180
Secondary, free: one band	~2.92	(m)	~3450
Secondary, bonded: one band	3.0-3.2	(m)	3320-3140
c. N—H Bending vibrations			
Primary amides, dilute solution	6.17-6.29	(s)	1620-1590
Secondary amides, dilute solution	6.45-6.62	(s)	1550-1510
C. Miscellaneous chromophoric groups			
1. ALCOHOLS AND PHENOLS			
a. O—H Stretching vibrations			
Free O—H	2.74-2.79	(v. sh)	3650-3590
Intermolecularly hydrogen bonded (change on dilution)			
single bridge compounds	2.82-2.90	(v. sh)	3550-3450
polymeric association	2.94-3.13	(s, b)	3400-3200
Intramolecularly hydrogen bonded (no change on dilution)			
single bridge compounds	2.80-2.90	(v. sh)	3570-3450
chelate compounds	3.1-4.0	(w, b)	3200-2500

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately.

## CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range $\mu$	Intensity	Range $\text{cm}^{-1}$
b. O—H Bending and C—O stretching vibrations			
Primary alcohols	~9.5 and 7.4-7.9	(s)	~1050 1350-1260
Secondary alcohols	~9.1 and 7.4-7.9	(s)	~1100 1350-1260
Tertiary alcohols	~8.7 and 7.1-7.6	(s)	~1150 1410-1310
Phenols	~8.3 and 7.1-7.6	(s)	~1200 1410-1310
2. AMINES			
a. N—H Stretching vibrations			
Primary, free; two bands	~2.86 and ~2.94	(m)	~3500 ~3400
Secondary, free; one band	2.86-3.02	(m)	3500-3310
Imines (=N—H); one band	2.94-3.03	(m)	3400-3300
Amine salts	3.2-3.3	(m)	3130-3030
b. N—H Bending vibrations			
Primary	6.06-6.29	(s-m)	1650-1590
Secondary	6.06-6.45	(w)	1650-1550
Amine salts	6.25-6.35 and ~6.67	(s)	1600-1575 ~1500
c. C—N Vibrations			
Aromatic, primary	7.46-8.00	(s)	1340-1250
Aromatic, secondary	7.41-7.81	(s)	1350-1280
Aromatic, tertiary	7.36-7.64	(s)	1360-1310
Aliphatic	8.2-9.8 and ~7.1	(w)	1220-1020 ~1410
3. UNSATURATED NITROGEN COMPOUNDS			
a. C $\equiv$ N Stretching vibrations			
Alkyl nitriles	4.42-4.46	(m)	2260-2240
$\alpha,\beta$ -Unsaturated alkyl nitriles	4.47-4.51	(m)	2235-2215
Aryl nitriles	4.46-4.50	(m)	2240-2220
Isocyanates	4.40-4.46	(m)	2275-2240
Isocyanides	4.50-4.83	(m)	2220-2070
b. C=N— Stretching vibrations (imines, oximes)			
Alkyl compounds	5.92-6.10	(v)	1690-1640
$\alpha,\beta$ -Unsaturated compounds	6.02-6.14	(v)	1660-1630
c. —N=N— Stretching vibrations, azo compounds	6.14-6.35	(v)	1630-1575
d. —N=C=N— Stretching vibrations, diimides	4.64-4.70	(s)	2155-2130
e. —N <sub>3</sub> Stretching vibrations, azides	4.63-4.72 and 7.46-8.48	(s)	2160-2120 1340-1180

## CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS†

Group	Range $\mu$	Intensity	Range $\text{cm}^{-1}$
f. C—NO <sub>2</sub> , Nitro compounds:			
aromatic	6.37-6.67 and 7.30-7.70	(s)	1570-1500 1370-1300
aliphatic	6.37-6.45 and 7.25-7.30	(s)	1570-1550 1380-1370
g. O—NO <sub>2</sub> , Nitrates	6.06-6.25 and 7.70-8.00	(s)	1650-1600 1300-1290
h. C—NO, Nitroso compounds	6.25-6.67	(s)	1600-1500
i. O—NO, Nitrites	5.95-6.06 and 6.15-6.21	(s)	1680-1650 1625-1610
4. HALOGEN COMPOUNDS, C—X STRETCHING VIBRATIONS			
a. C—F	7.1-10.0	(s)	1400-1000
b. C—Cl	12.5-16.6	(s)	800-600
c. C—Br	16.6-20.0	(s)	600-500
d. C—I	~20	(s)	~500
5. SULFUR COMPOUNDS			
a. S—H Stretching vibrations	3.85-3.92	(w)	2600-2550
b. C=S Stretching vibrations	8.33-9.52	(s)	1200-1050
c. S=O Stretching vibrations:			
sulfoxides	9.35-9.71	(s)	1070-1030
sulfones	8.62-8.77	(s)	1160-1140
	and 7.41-7.69	(s)	1350-1300
sulfites	8.13-8.70	(s)	1230-1150
	and 7.00-7.21	(s)	1430-1350
sulfonyl chlorides	8.44-8.59	(s)	1185-1165
	and 7.30-7.46	(s)	1370-1340
sulfonamides	8.48-8.77	(s)	1180-1140
	and 7.41-7.69	(s)	1350-1300
sulfonic acids	8.27-8.70	(s)	1210-1150
	9.43-9.71	(s)	1060-1030
	and ~15.4	(s)	~650

† Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp, ~ = approximately



Proton Chemical Shifts (Values are given on the officially approved  $\delta$  scale;  $\tau = 10.00 - \delta$ )

1

Substituent Group	Methyl Protons	Methylene Protons	Methine Proton
HC-C-CH <sub>2</sub>	0.95	1.20	1.55
HC-C-NR <sub>2</sub>	1.05	1.45	1.70
HC-C-C=C	1.00	1.35	1.70
HC-C-C=O	1.05	1.55	1.95
HC-C-NR <sub>2</sub> Ar	1.10	1.50	1.80
HC-C-NH(C=O)R	1.10	1.50	1.90
HC-C-(C=O)NR <sub>2</sub>	1.10	1.50	1.80
HC-C-(C=O)Ar	1.15	1.55	1.90
HC-C-(C=O)OR	1.15	1.70	1.90
HC-C-Ar	1.15	1.55	1.80
HC-C-OH (and OR)	1.20	1.50	1.75
HC-C-C≡CR	1.20	1.50	1.80
HC-C-C≡N	1.25	1.65	2.00
HC-C-SR	1.25	1.60	1.90
HC-C-OAr	1.30	1.55	2.00
HC-C-O(C=O)R	1.30	1.60	1.80
HC-C-SH	1.30	1.60	1.65
HC-C-(S=O)T and -SO <sub>2</sub> R	1.35	1.70	2.05
HC-C-NR <sub>3</sub> <sup>+</sup>	1.40	1.75	2.05
HC-C-O(C=O)CF <sub>3</sub>	1.40	1.65	1.95
HC-C-Cl	1.55	1.80	1.85
HC-C-O(C=O)Ar	1.65	1.75	1.90
HC-C-Br	1.80	1.85	1.50
HC-C-CH <sub>2</sub>	0.90	1.30	1.50
HC-C=C	1.60	2.05	2.80
HC-C≡C	1.70	2.20	2.50
HC-(C=O)OR (and NR <sub>2</sub> )	2.00	2.25	3.00
HC-SR	2.05	2.55	2.65
HC-O-O	2.10	2.30	2.90
HC-(C=O)R	2.10	2.35	2.65
HC-C≡N	2.15	2.45	2.90
HC-C-CHO	2.20	2.40	2.85
HC-Ar (and NR <sub>2</sub> )	2.25	2.45	3.40
HC-SSR	2.25	2.70	3.40
HC-(C=O)Ar	2.40	2.70	3.60
HC-SAr	2.40	3.10	4.10
HC-NR <sub>2</sub> Ar	2.60	3.05	3.85
HC-SO <sub>2</sub> R and -(SO)R	2.60	3.40	3.60
HC-Br	2.70	3.10	4.10
HC-NR <sub>3</sub> <sup>+</sup>	2.95	3.35	3.85
HC-NH(C=O)R	2.95	3.45	4.05
HC-Cl	3.05	3.40	3.60
HC-OH and -OR	3.20	3.75	4.05
HC-NH <sub>2</sub>	3.50	4.10	4.95
HC-O(C=O)R	3.65	4.00	4.60
HC-OAr	3.80	4.20	5.05
HC-O(C=O)Ar	3.80	4.20	5.05


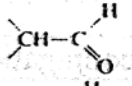
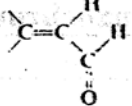



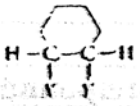


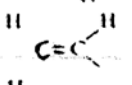
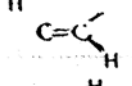
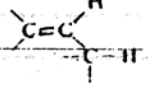
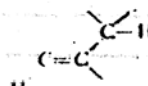
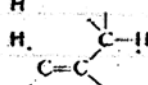
Substituent Group	Methyl Protons	Methylene Protons	Methine Proton
HC-F	4.25	4.50	4.80
HC-NO <sub>2</sub>	4.30	4.35	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	

Substituent Group	Proton Shift	Substituent Group	Proton Shift
HC≡CH	2.35	HO-C=O	10-12
HC≡CAr	2.90	HO-SO <sub>2</sub>	11-12
HC≡C-C=C	2.75	HO-Ar	4.5-6.5
HAr	7.20	HO-R	0.5-4.5
HCO-O	8.1	HS-Ar	2.8-3.6
HCO-R	9.4-10.0	HS-R	1-2
HCO-Ar	9.7-10.5	HN-Ar	3-6
HO-N=C(oxime)	9-12	HN-R	0.5-5

<sup>13</sup>C Chemical Shifts (Values given on the  $\delta$  scale, relative to TMS.)

Substituent Group	Primary Carbon	Secondary Carbon	Tertiary Carbon	Quaternary Carbon
Alkanes				
C-C≡	-20 to 30	25 to 45	30 to 60	35 to 70
C-O	40 to 60	40 to 70	60 to 75	70 to 85
C-N	20 to 45	40 to 60	50 to 70	65 to 75
C-S	10 to 30	25 to 45	40 to 55	55 to 70
C-Halide	-37 to 35	-10 to 45	30 to 65	85 to 75
	(1) (Cl)	(1) (Cl)	(1) (Cl)	(1) (Cl)
Alkynes	70 to 100	Isocyanides		130 to 150
Alkenes	110 to 150	Carbonates		150 to 160
Aromatics	110 to 135	Oximes		155 to 165
C-substituted	125 to 145	Ureas		150 to 170
Heteroaromatics	115 to 140	Thioureas		165 to 185
C- $\alpha$	135 to 155	Esters, Anhydrides		150 to 175
Cyanates	105 to 120	Amides		160 to 185
Isoyanates	115 to 135	Acids, Acyl chlorides		160 to 185
Thiocyanates	110 to 120	Aldehydes		175 to 205
Isothiocyanates	120 to 140	Ketones		175 to 225
Cyanides	110 to 130			

SPIN-SPIN COUPLING CONSTANTS			
Type	J, cps	Type	J, cps
$H_2^t$	280	$C=CH-CH=C$	9-13
$CH_2^t$	12.4	$H-C\equiv C-H^t$	9.1
	12-15	$CH-C\equiv C-H$	2-3
$CH-CH$	2-9		1-3
$-C-(C)_n-C-$	~0		6-8
$CH_2-CH_2-X$	6.5-7.5		$o$ - 6-9 $m$ - 1-3 $p$ - 0-1
$CH_2-N$	5.5-7.0		$\alpha\beta$ 1.6-2.0 $\alpha\beta'$ 0.6-1.0 $\alpha\alpha'$ 1.3-1.8 $\beta\beta'$ 3.2-3.8
$CH_2$			$\alpha\beta$ 2.0-2.6 $\alpha\beta'$ 1.5-2.2 $\alpha\alpha'$ 1.8-2.3 $\beta\beta'$ 2.8-4.0
	$a,a$ 5-10 $a,c$ 2-4 $c,c$ 2-4		$\alpha\beta$ 4.6-5.8 $\alpha\beta'$ 1.0-1.8 $\alpha\alpha'$ 2.1-3.3 $\beta\beta'$ 3.0-4.2
$C=C$	0.5-3		$\alpha\beta$ 4.9-5.7 $\alpha\gamma$ 1.6-2.6 $\alpha\beta'$ 0.7-1.1 $\alpha\alpha'$ 0.2-0.5 $\beta\gamma$ 7.2-8.5 $\beta\beta'$ 1.4-1.9
	7-12		
	13-18		
	4-10		
	0.5-2.5		
	~0		

TURN OVER

## Conjugated dienes &amp; Trienes, Solvent: Ethanol

Parent value for Butadiene system or acyclic conjugated diene	217 nm
Acyclic triene	245 nm
Homoannular conjugated diene	253 nm
Heteroannular conjugated diene	215 nm
Increment for each substituents	
Alkyl substituents or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Auxochrome	
-OR	+6 nm
-SR	+30 nm
-Cl, -Br	+5 nm
NR <sub>2</sub>	+60 nm
-OCOCH <sub>3</sub>	0

Woodward Fieser rules for  $\alpha\beta$ -unsaturated carbonyl compounds:-

<b>a) Parent values</b>			
$\alpha\beta$ -unsaturated acyclic or six membered ketone	215 nm		
$\alpha\beta$ -unsaturated five membered ring ketone	202 nm		
$\alpha\beta$ -unsaturated aldehyde	207 nm		
<b>b) Increments</b>			
<b>i) Each alkyl substituents or ring residue</b>			
At $\alpha$ position	10 nm		
At $\beta$ position	12 nm		
At gamma and higher position	18 nm		
<b>ii) Each exocyclic double bond</b>			
5 nm			
<b>iii) Double bond extending conjugation</b>			
30 nm			
<b>iv) Homoannular conjugated diene</b>			
39 nm			
<b>Auxochromes</b>	<b>Positions</b>		
	$\alpha$	$\beta$	gamma
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
-OCOCH <sub>3</sub>	6	6	6
-Cl	15	12	-
-Br	25	30	-
-NR <sub>2</sub>	-	95	-