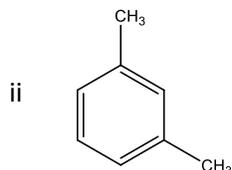


Please check whether you have got the right question paper.

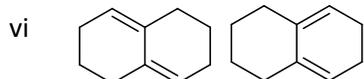
- N.B: (1) All questions are compulsory  
 (2) Figures to the right indicate full marks  
 (3) Answer all the sub-questions together and in order  
 (4) Spectral correlation tables are allowed

Q1) a) Answer any four ( 1 mark each) 4

- i Calculate the index of hydrogen deficiency for  $C_{10}H_{14}N_2$   
 Predict the number of signals in the  $^{13}C$  NMR of

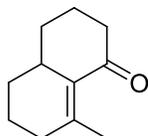


- iii Predict the number of signals in the  $^1H$  NMR of  $Cl_2CHCH_2Br$   
 iv Draw structure of the ion responsible for peak at  $m/z=46$  in the mass spectrum of 2-butanol .  
 v Predict two characteristic IR frequencies of benzoic acid.  
 Name a simple spectroscopic technique which will help distinguish between

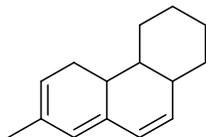


Q.1) b) Answer any **eight** (two marks each) 16

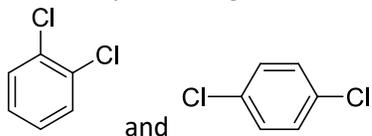
- i Predict the UV  $\lambda_{max}$  for



- ii Predict the UV  $\lambda_{max}$  for



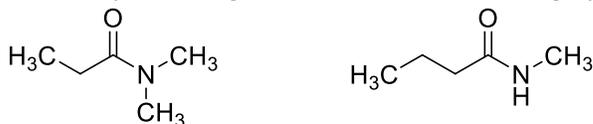
- iii How will you distinguish between the following by  $^{13}C$  NMR spectroscopy?



iv How will you distinguish between the following compounds by IR spectroscopy?



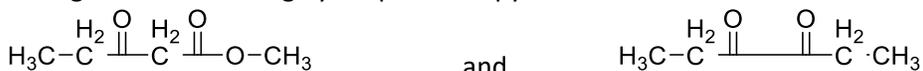
v How will you distinguish between the following by mass spectrometry?



vi Depict two fragmentation pathways for 1-phenyl 1-propanone.

vii Predict the  $^1\text{H}$  NMR spectrum of toluene giving  $\delta$  values, splitting pattern and ratio number of proton intensities.

viii Distinguish the following by IR spectroscopy-



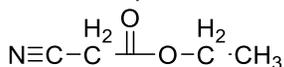
ix In benzaldehyde, two of the ring protons have resonance at 7.87 ppm, and the other three have resonance in the range from 7.5 to 7.6 ppm. Explain.

x Assign the vibrations for the following IR bands, 1550 and 1745  $\text{cm}^{-1}$ .

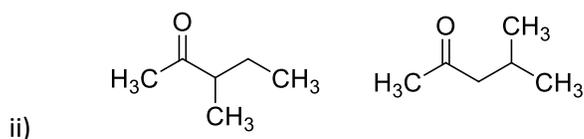
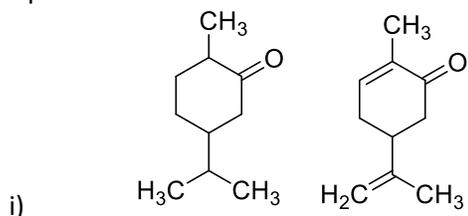
Q.2 Answer any five questions (5 × 7)

35

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



b) How will you distinguish between following compounds using any one spectral technique. Give distinguishing spectral characteristics. If mass spectrometry is used one fragmentation pathway has to be depicted.



c) A compound with molecular formula  $\text{C}_4\text{H}_8\text{O}_2$  has the following spectral data

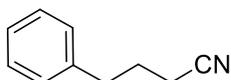
IR: 2983, 1743, 1243  $\text{cm}^{-1}$

$^1\text{H}$  NMR  $\delta$  4.3 (q), 2.1 (s), 1.2 (t)

Deduce the structure and depict one mass fragmentation pathway.

**Q.P. Code :21420**

- d) An organic compound containing C, H and O, has molecular weight 150 and has characteristic IR bands at 1680, and 1250-1000 and  $^1\text{H}$  NMR at  $\delta$  7.8 (d, 2 sq),  $\delta$  7 (d, 2sq),  $\delta$  3.9 (s, 3sq),  $\delta$  2.6 (s, 3sq). The  $^{13}\text{C}$ -NMR shows 7 types of C at 200, 163, 131, 130, 114, 55 and 26 ppm. Predict its structure and justify your answer.
- e) Compound with molecular formula  $\text{C}_5\text{H}_{12}\text{O}$  has following spectral characteristics  
 $^1\text{H}$  NMR Shift ppm (splitting, Area) : 2.4(s:D<sub>2</sub>O exchangeable,1sq), 1.4(q,2sq), 1.1(s, 6), 0.8(t,3sq)  
 Deduce the structure and predict  $^{13}\text{C}$  NMR for the same.
- f) Predict the  $^1\text{H}$  NMR and mass spectrum of the following compound



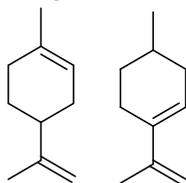
Depict two fragmentation pathways for the molecule one involving fission and the other rearrangement.

- g) A compound, with formula  $\text{C}_5\text{H}_8\text{O}_4$ , shows strong absorption at  $1734\text{ cm}^{-1}$  and  $1745\text{ cm}^{-1}$ . Also it has several strong bands centering at about  $1200\text{ cm}^{-1}$  in the infrared spectrum. The  $^1\text{H}$  NMR shows following characteristic signals.  
 $^1\text{H}$  NMR  $\delta$  4.2 (q) , 3.4(s), 1.3(t)  
 Draw its structure.

Q.3) Answer any five questions (4 marks each)

20

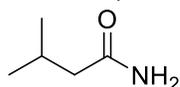
- a) Distinguish between the following compounds using suitable spectral techniques



- b) Identify the compound with molecular formula  $\text{C}_{10}\text{H}_{14}$  showing following spectral information

$^1\text{H}$ NMR	7.2 (4H, s), 2.6(2H,q),1.25(3H, t)
$^{13}\text{C}$ NMR	141,127, 28, 15

- c) How will you distinguish between cis and trans isomers of  $\text{CH}_3\text{CH}=\text{CHCOOH}$ .
- d) Draw the structure a compound having molecular weight 116, which meet the following  
 (i)  $^1\text{H}$ NMR data-  $\delta$  11 (1H, s),  $\delta$  2.6 (4H, t),  $\delta$  2.12 (3H, s)  
 (ii) IR : 3333-2850, 2965, 1715,  $1200\text{ cm}^{-1}$
- e) Predict IR,  $^{13}\text{C}$ NMR spectra for 3-Methylbutanamide.



- f) A compound with molecular formula  $\text{C}_8\text{H}_8\text{O}$  show  $^1\text{H}$  NMR signals at  $\delta$  8.1 (t), 7.2(s), 2.6(d) ppm. The IR bands are seen at 1720, 2800-2710 and  $1600\text{--}1500\text{ cm}^{-1}$ . Identify the structure and justify.
- g) Depict the fragmentation pathways in mass spectroscopy one by fission and another by rearrangement for heptanal.

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SPECTRAL CORRELATION TABLES

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

GROUP	-Cl	-CO	-OC	-F	-O	-S	-N	-I	-OH	-OR	-OPh	-OC(=O)R	-Cl(O)R	-Cl(O)Ph	-Cl(O)OR	-Cl(O)NR <sub>2</sub>	-ON	-NR <sub>2</sub>	-NHC(=O)R	-N <sub>3</sub>	-SR
-Cl	1.17	1.90	2.14	2.55	1.91	1.84	3.23	3.33	3.30	3.70	3.40	4.25	2.47	2.54	2.25	2.23	2.40	2.27	2.97	2.67	2.34
-CO	2.60	3.39	3.30	3.40	2.76	2.69	4.08	3.88	3.37	3.19	3.91	4.78	4.48	3.28	3.38	3.10	3.74	3.25	3.13	3.82	3.52
-OC	3.11	3.52	2.88	2.81	4.20	4.00	3.49	4.28	4.03	4.90	4.90	4.71	3.37	3.51	3.22	3.26	3.37	3.24	3.97	3.67	3.31
-F	3.27	3.50	4.20	4.35	4.70	4.70	3.91	3.08	3.35	3.40	4.01	4.70	3.91	3.08	3.35	3.40	3.65	3.48	3.97	3.67	3.31
-O	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	3.78	3.65	4.34	4.04	3.72
-S	2.63	2.58	3.97	3.76	3.26	4.01	3.80	4.47	4.57	3.12	3.28	2.99	3.03	3.12	3.01	3.71	3.41	3.01	3.41	3.01	3.01
-N	3.51	3.90	3.70	3.19	3.93	4.73	4.80	4.54	5.07	5.21	2.97	2.96	3.07	2.94	3.07	2.94	3.64	3.34	3.01	3.01	3.01
-I	4.99	5.16	4.99	5.40	5.99	5.89	4.46	4.60	4.31	4.35	4.46	4.40	4.31	4.35	4.46	4.37	5.19	4.73	4.40	4.40	4.40
-OH	4.29	4.09	4.58	5.32	5.12	5.79	5.69	4.26	3.40	4.11	4.15	4.26	4.13	4.26	4.13	4.26	4.13	4.26	4.13	4.26	4.13
-OR	3.90	3.87	4.61	4.41	3.18	3.06	3.75	3.89	3.60	3.64	3.75	3.64	3.65	3.65	3.62	4.32	4.02	3.69	3.69	3.69	3.69
-OPh	4.55	4.35	4.11	6.05	5.95	4.49	4.63	4.34	4.38	4.49	4.35	5.06	4.78	4.43	4.13	4.20	4.15	4.94	4.84	4.84	4.84
-OC(=O)R	4.95	5.8	5.72	4.59	4.43	5.32	5.18	4.29	4.45	4.45	4.45	4.45	4.45	4.45	4.45	4.45	4.45	4.45	4.45	4.45	4.45
-Cl(O)R	6.69	6.39	5.16	5.30	5.09	4.05	5.16	5.03	5.86	5.36	5.10	4.42	5.10	4.91	3.95	5.10	4.92	5.63	5.37	5.00	5.00
-Cl(O)Ph	3.60	3.63	3.77	3.48	3.62	3.63	3.30	4.20	3.90	3.57	3.60	3.60	3.60	3.60	3.60	3.60	3.60	3.60	3.60	3.60	3.60
-Cl(O)OR	3.91	3.62	3.66	3.77	3.64	4.34	4.02	3.71	3.35	3.37	3.48	3.35	3.37	3.48	3.35	3.37	3.48	3.35	3.37	3.48	3.35
-Cl(O)NR <sub>2</sub>	3.33	3.37	3.48	3.35	4.05	3.75	3.42	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30
-ON	3.41	3.52	3.39	4.09	3.79	3.46	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30
-NR <sub>2</sub>	3.53	3.50	4.20	3.90	3.57	3.10	3.37	4.07	3.77	3.44	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30
-NHC(=O)R	3.37	4.07	3.77	3.44	4.75	4.45	4.14	4.15	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84
-N <sub>3</sub>	4.15	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84	3.84
-SR	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51	3.51

TURN OVER



CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range, $\text{cm}^{-1}$	Intensity	Range, $\text{cm}^{-1}$	Intensity
Unsaturated vinyl ether type	3.56-5.65	(s)	1800-1770	(s)
$\alpha,\beta$ -unsaturated aldehyde	5.78-5.82	(s)	1730-1717	(s)
$\alpha,\beta$ -unsaturated ketone	5.78-5.82	(s)	1730-1717	(s)
$\alpha,\beta$ -unsaturated lactone	5.65-5.75	(s)	1760-1740	(s)
$\beta,\gamma$ -unsaturated lactone	5.56	(s)	~1800	(s)
$\alpha$ -Ketoesters	5.70-5.75	(s)	1755-1740	(s)
$\beta$ -Ketoesters (enol)	6.06	(s)	~1850	(s)
Carbonates	5.62-5.75	(s)	1785-1740	(s)
<b>4. CARBOXYLIC ACIDS</b>				
a. Carbonyl stretching vibrations saturated aliphatic	5.80-5.88	(s)	1715-1700	(s)
$\alpha,\beta$ -unsaturated aliphatic aryl	5.83-5.92	(s)	1715-1690	(s)
b. Carbonyl stretching (bonded) several bands	3.70-4.00	(w)	2700-2500	(w)
c. Carboxylate anion stretching	6.21-6.45	(s)	1610-1550	(s)
and	7.15-7.69	(s)	1400-1300	(s)
<b>5. ANHYDRIDE STRETCHING VIBRATIONS</b>				
a. Saturated acyclic	5.41-5.56	(s)	1830-1800	(s)
and	5.59-5.75	(s)	1790-1740	(s)
b. $\alpha,\beta$ -Unsaturated aryl acyclic	5.47-5.62	(s)	1830-1780	(s)
and	5.65-5.81	(s)	1770-1720	(s)
c. Saturated 5-membered ring	5.35-5.49	(s)	1870-1820	(s)
d. $\alpha,\beta$ -Unsaturated 5-membered ring	5.41-5.56	(s)	1860-1750	(s)
and	5.47-5.62	(s)	1830-1780	(s)
<b>6. ACYL HALIDE STRETCHING VIBRATIONS</b>				
a. Acyl fluorides	~5.41	(s)	~1850	(s)
b. Acyl chlorides	~5.57	(s)	~1795	(s)
c. Acyl bromides	~5.53	(s)	~1810	(s)
d. $\alpha,\beta$ -Unsaturated aryl	5.61-5.72	(s)	1780-1750	(s)
and	5.72-5.82	(m)	1750-1720	(m)
e. COF <sub>2</sub>	5.19	(s)	1928	(s)
f. COCl <sub>2</sub>	5.47	(s)	1828	(s)
g. COBr <sub>2</sub>	5.47	(s)	1828	(s)
<b>7. AMIDES</b>				
a. Carbonyl stretching vibrations solution	~6.06	(s)	~1650	(s)
Primary, dilute solution	~5.92	(s)	~1690	(s)
Secondary, solid and concentrated solution	5.95-6.14	(s)	1630-1630	(s)
Tertiary, solid and all solutions	5.88-5.99	(s)	1700-1670	(s)
Cyclic $\beta$ -lactams, dilute solution	5.99-6.24	(s)	1670-1630	(s)
Cyclic $\gamma$ -lactams, dilute solution	~5.95	(s)	~1680	(s)
and	~5.88	(s)	~1700	(s)

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range, $\text{cm}^{-1}$	Intensity	Range, $\text{cm}^{-1}$	Intensity
Cyclic $\gamma$ -lactams, fused to another ring, dilute solution	5.71-5.88	(s)	1750-1700	(s)
Cyclic $\beta$ -lactams, dilute solution	5.68-5.78	(s)	1760-1720	(s)
Cyclic $\beta$ -lactams, fused to another ring, dilute solution	5.62-5.65	(s)	1780-1770	(s)
Ureas, acyclic	~6.02	(s)	~1660	(s)
Ureas, cyclic, 6-membered ring	~6.10	(s)	~1640	(s)
Ureas, cyclic, 5-membered ring	~5.81	(s)	~1730	(s)
Urethanes	5.75-5.92	(s)	1740-1690	(s)
Imides, acyclic	~5.85	(s)	~1710	(s)
and	~5.88	(s)	~1700	(s)
Imides, cyclic, 6-membered ring	~5.85	(s)	~1710	(s)
and	~5.88	(s)	~1700	(s)
Imides, cyclic, $\alpha,\beta$ -unsaturated, 6-membered ring	~5.78	(s)	~1730	(s)
and	~5.99	(s)	~1670	(s)
Imides, cyclic, 5-membered ring	~5.65	(s)	~1770	(s)
and	~5.88	(s)	~1700	(s)
Imides, cyclic, $\alpha,\beta$ -unsaturated, 5-membered ring	~5.59	(s)	~1790	(s)
and	~5.85	(s)	~1710	(s)
N-H Stretching vibrations				
a. Primary, free; two bands	~2.86	(m)	~3500	(m)
and	~2.94	(m)	~3400	(m)
Primary, bonded; two bands	~2.99	(m)	~3350	(m)
and	~3.15	(m)	~3180	(m)
Secondary, free; one band	~2.92	(m)	~3430	(m)
Secondary, bonded; one band	3.0-3.2	(m)	3330-3140	(m)
N-H Bending vibrations				
a. Primary amides, dilute solution	6.17-6.29	(s)	1620-1590	(s)
Secondary amides, dilute solution	6.45-6.62	(s)	1550-1510	(s)
<b>C. MISCELLANEOUS CHROMOPHORE GROUPS</b>				
<b>1. ALCOHOLS AND PHENOLS</b>				
a. O-H Stretching vibrations Free O-H	2.74-2.79	(v. sh)	3650-3590	(v. sh)
Intermolecularly hydrogen bonded (change on dilution)				
single bridge compounds	2.82-2.90	(v. sh)	3550-3450	(v. sh)
polymeric association	2.94-3.13	(s, b)	3400-3200	(s, b)
intramolecularly hydrogen bonded (no change on dilution)				
single bridge compounds	2.80-2.90	(v. sh)	3570-3490	(v. sh)
chelate compounds	3.1-4.0	(v. b)	3200-2500	(v. b)

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

TURN OVER

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range, $\mu$	Intensity	Range, $\text{cm}^{-1}$
<b>1. O—H Bending and C—O stretching vibrations</b>			
Primary alcohols	and -9.5 7.4-7.9	(s)	-1050 1350-1260
Secondary alcohols	and -9.1 7.4-7.9	(s)	-1100 1350-1260
Tertiary alcohols	and -8.7 7.1-7.6	(s)	-1150 1410-1310
Phenols	and -8.3 7.1-7.6	(s)	-1200 1410-1310
<b>2. AMINES</b>			
<b>a. N—H Stretching vibrations</b>			
Primary, free; two bands	and -7.86 -7.94	(m)	-3500 -3400
Secondary, free; one band	2.86-3.02	(m)	3400-3310
Imines (=N—H); one band	2.94-3.03	(m)	3400-3300
Amine salts	3.2-3.3	(m)	3130-3030
<b>b. N—H Bending vibrations</b>			
Primary	6.06-6.29	(s-m)	1650-1590
Secondary	6.06-6.45	(w)	1650-1550
Amine salts	6.25-6.35	(s)	1600-1575
and	-6.67	(s)	-1500
<b>c. C—N Vibrations</b>			
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	8.2-9.3	(w)	1220-1020
and	-7.1	(w)	-1410
<b>3. UNSATURATED NITROGEN COMPOUNDS</b>			
<b>a. C≡N Stretching vibrations</b>			
Alkyl nitriles	4.2-4.46	(m)	2260-2240
$\alpha,\beta$ -Unsaturated alkyl nitriles	4.47-4.51	(m)	2235-2215
Aryl nitriles	4.46-4.50	(m)	2240-2220
Isoocyanates	4.40-4.46	(m)	2275-2240
Isoocyanides	4.50-4.83	(m)	2220-2070
<b>b. C=N— Stretching vibrations (imines, oximes)</b>			
Alkyl compounds	5.92-6.10	(v)	1600-1640
$\alpha,\beta$ -Unsaturated compounds	6.02-6.14	(v)	1650-1650
<b>c. —N=N— Stretching vibrations, azo compounds</b>			
—N=C=N— Stretching vibrations, diazides	6.14-6.35	(v)	1630-1575
—N=N— Stretching vibrations, azides	4.64-4.70	(s)	2155-2130
—N <sub>2</sub> Stretching vibrations, azides	4.63-4.72	(s)	2160-2120
and	7.46-8.48	(w)	1340-1180

TURN OVER

CHARACTERISTIC INFRARED ABSORPTIONS OF FUNCTIONAL GROUPS

Group	Range, $\mu$	Intensity	Range, $\text{cm}^{-1}$
<b>f. C—NO<sub>2</sub>, Nitro compounds; aromatic</b>			
	and 6.37-4.67 7.30-7.70	(s)	1570-1500
aliphatic	and 5.37-6.45 7.25-7.30	(s)	1370-1300
	and 6.06-6.25 7.70-8.00	(s)	1570-1590
<b>g. O—NO<sub>2</sub>, Nitrates</b>			
	and 6.35-6.67 5.95-6.06	(s)	1650-1600
	and 6.15-6.21	(s)	1600-1500
		(s)	1680-1650
		(s)	1625-1610
<b>4. HALOGEN COMPOUNDS, C—X STRETCHING VIBRATIONS</b>			
<b>a. C—F</b>	7.1-10.0	(s)	1400-1000
<b>b. C—Cl</b>	12.5-16.6	(s)	800-600
<b>c. C—Br</b>	16.6-20.0	(s)	600-500
<b>d. C—I</b>	-20	(s)	-500
<b>5. SULFUR COMPOUNDS</b>			
<b>a. S—H Stretching vibrations</b>			
<b>b. C=S Stretching vibrations</b>	3.85-3.92	(w)	2600-2550
<b>c. S=O Stretching vibrations; sulfoxides</b>	8.33-9.52	(s)	1200-1050
	9.35-9.71	(s)	1070-1030
	8.62-8.72	(s)	1160-1140
	and 7.81-7.69	(s)	1350-1300
	8.13-8.70	(s)	1230-1150
<b>sulfites</b>	and 7.00-7.41	(s)	1430-1350
	8.44-8.59	(s)	1185-1165
<b>sulfonyl chlorides</b>	and 7.30-7.46	(s)	1370-1340
<b>sulfonamides</b>	8.48-8.77	(s)	1180-1140
<b>sulfonic acids</b>	and 7.41-7.69	(s)	1350-1300
	8.27-8.70	(s)	1210-1150
	9.43-9.71	(s)	1060-1030
and	-15.4	(s)	-650

f 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;  $\tau = 10.00 - \delta$ )

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

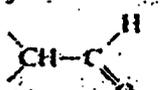
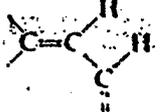
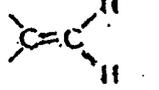
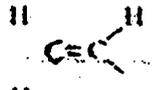
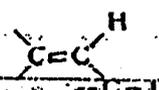
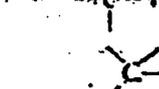
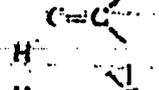
Substituent Group	Methyl Protons	Methylene Protons	Methine Protons
HC-F	4.25	4.50	4.80
HC-NO <sub>2</sub>	4.30	4.55	4.60
Cyclopropane		0.20	0.40
Cyclobutane		2.45	
Cyclopentane		1.65	
Cyclohexane		1.50	1.80
Cycloheptane		1.25	
Substituent Group	Proton Shift	Substituent Group	Proton Shift
HC≡CH	2.35	HO-C=O	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
HA	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(O)Ar	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=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	45 to 75
	(I) (Cl)	(I) (Cl)	(I) (Cl)	(I) (Cl)
Substituent Group	Primary Carbon	Secondary Carbon	Tertiary Carbon	Quaternary Carbon
Alkenes	70 to 100	Isocyanides		130 to 150
Alkynes	110 to 150	Carbonates		150 to 160
Aromatics	110 to 135	Carbamates		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 180
Isocyanates	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			

TURN OVER

SPIN-SPIN COUPLING CONSTANTS

Type	J, cps	Type	J, cps
$H_3^+$	280	$C-CH=CH-C$	9-13
$CH_3^+$	12.4	$H-C\equiv C-H^+$	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		<i>o</i> -6-9 <i>m</i> -1-3 <i>p</i> -0-1
$CH-N$	5.5-7.0		<i>αβ</i> 1.6-2.0 <i>αβ'</i> 0.6-1.0 <i>αα'</i> 1.3-1.8 <i>ββ'</i> 3.2-3.8
$CH_2$	<i>α,α</i> 5-10 <i>α,c</i> 2-4 <i>c,c</i> 2-4		<i>αβ</i> 2.0-2.6 <i>αβ'</i> 1.5-2.2 <i>αα'</i> 1.8-2.3 <i>ββ'</i> 2.8-4.0
	0.5-3		<i>αβ</i> 4.6-5.8 <i>αβ'</i> 1.0-1.8 <i>αα'</i> 2.1-3.3 <i>ββ'</i> 3.0-4.2
	7-12		<i>αβ</i> 4.9-5.7 <i>αγ</i> 1.6-2.6
	13-18		<i>αβ</i> 0.7-1.1 <i>αα'</i> 0.2-0.5 <i>βγ</i> 7.2-8.5 <i>ββ'</i> 1.4-1.9
	4-10		
	<i>α,α'</i> 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:-

a) Parent values			
$\alpha\beta$ -unsaturated acyclic or six membered ketone	215 nm		
$\alpha\beta$ -unsaturated five membered ring ketone	202 nm		
$\alpha\beta$ -unsaturated aldehyde	207 nm		
b) Increments			
i) Each alkyl substituents or ring residue			
At $\alpha$ position	10 nm		
At $\beta$ position	12 nm		
At gamma and higher position	18 nm		
ii) Each exocyclic double bond	5 nm		
iii) Double bond extending conjugation	30 nm		
iv) Homoannular conjugated diene	39 nm		
Auxochromes	Positions		
	$\alpha$	$\beta$	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	-