KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2010/2011

OPEN, DISTANCE AND E-LEARNING EXAMINATION FOR THE DEGREE OF BACHELOR OF SCIENCE AND BACHELOR OF EDUCATION

SCH 311: ORGANIC SPECTROSCOPY

DATE: **Thursday 7th July 2011** **TIME:** **8.00a.m – 10.00a.m**

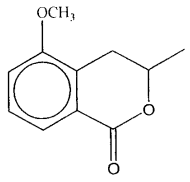
INSTRUCTIONS: Answer ALL Questions.
The spectroscopic tables are provided at the end.

1. (a) Calculate the frequency and wavenumber of infrared light of wavelength $\lambda = 10$ μm. [3 marks]

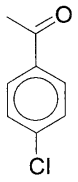
(b) For ultraviolet light of wavelength 200 nm, calculate:
(i) the frequency of this light,
(ii) the amount of energy absorbed by one molecule when it interacts with this light, and the corresponding amount of energy absorbed by one mole of substance. [3 marks]

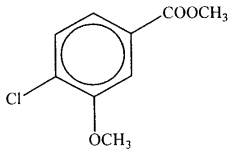
(c) Calculate the expected λ_{max} for the $\pi \longrightarrow \pi^*$ transitions or K-band for the following compounds using the Woodward, Fisher, Nielson and Scott rules. [10 marks]

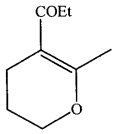
(i)



(ii)



(iii) 

(iv) 

2. Discuss what features of their IR spectra could help in distinguishing the following pairs? [8 marks]

(a) 4-(Aminomethyl)benzoic acid, $H_2NCH_2C_6H_4COOH$ and 4-aminophenylacetic acid, $H_2NC_6H_4CH_2COOH$.

(b) Butanamide, $CH_3CH_2CH_2CONH_2$ and N-methylpropanamide, $CH_3CH_2CONHCH_3$.

3. (a) How could IR spectroscopy be used to distinguish the members of the following pairs, and how reliable would these distinctions be? [6 Marks]
   (i) the *cis* and *trans* isomers of 3-hexene,
   (ii) natural rubber (*cis*-polyisoprene) and butyl rubber (polyisobutene), and
   (iii) 1-hexyne and 3-hexyne?

(b) Explain with examples the following: [6 marks]
   (i) Overtones
   (ii) Finger print region
   (i) Fermi resonance

4. (a) Assign structures to each of the compounds (**A**, **B** and **C**) in the following **Figure 1**. [9 marks]

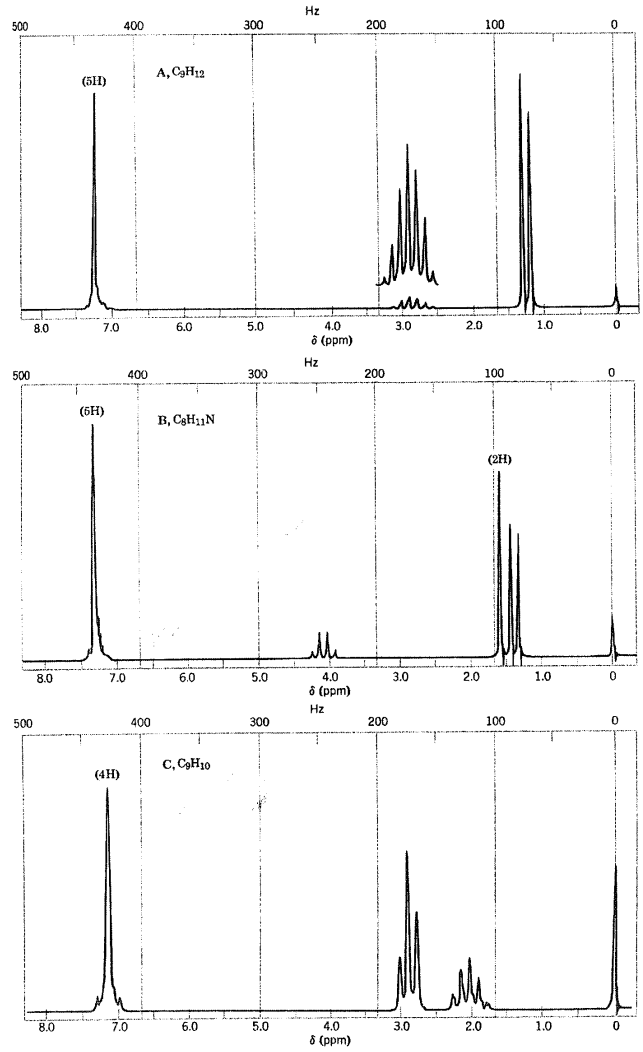


Figure 1. ^{1}H NMR spectra.

(b) the proton-decoupled ^{13}C spectrum given in **Figure 2** is of a tribromobenzene, $C_6H_3Br_3$. Which tribromobenzene is it? [6 marks]

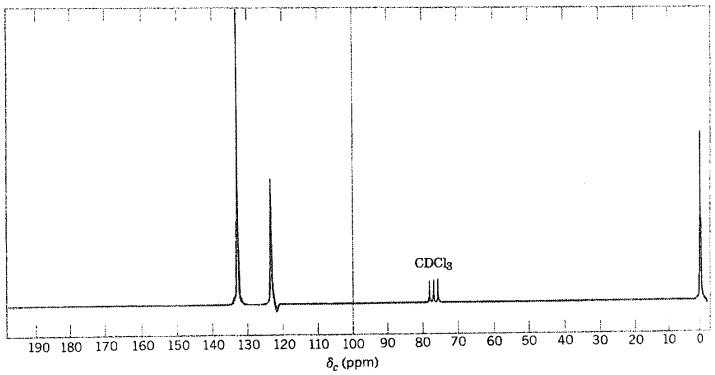


Figure 2. ^{13}C spectrum of a tribromobenzene.

5. (a) Calculate the expected apparent mass fo the metastable ion produced when *m/z* 77 decomposes by loss of CH≡CH to *m/z* 51. [3 Marks]

(b) Predict the structure of the base peak in the mass spectrum of (a) *n*-octane and (b) 2-methylpentane. [4 Marks]

6. Assign possible structure with suitable reasons to an organic compound whose spectral data is given below: [12 Marks]

UV λ_{max}^{EtOH} 295 nm

IR $\nu_{max}^{liq.}$: 1715 (s), 2900-2700, cm^{-1}.

^1H NMR: δ 2.4 (2H, q), 2.09 (3H, s), 1.04 (3H, t).

^{13}C NMR: (proton noise decoupled) δ 208.79, 36.80, 29.37, 7.86.
(off-resonance) δ 208.79, 36.80, 29.37, 7.86.

MS (% rel.): 72 ($M^{+\cdot}$, 23%), 57 (9%), 43 (100%), 29 (18%).

Table 1. Rules for the principal band of substituted benzene derivatives R—C_6H_4—COX

	Orientation	λ_{calc}^{EtOH}, *nm*
Parent chromophore:		
X = alkyl or ring residue		**246**
X = H		**250**
X = OH or OAlkyl		**230**
Increment for each substituent:		
R = alkyl or ring residue	*o, m*	**3**
	p	**10**
R = OH, OMe, OAlkyl	*o, m*	**7**
	p	**25**
R = O^-	*o*	**11**
	m	**20**
	p	**78**
R = Cl	*o, m*	**0**
	p	**10**
R = Br	*o, m*	**2**
	p	**15**
R = NH_2	*o, m*	**13**
	p	**58**
R = NHAc	*o, m*	**20**
	p	**45**
R = NHMe	*p*	**73**
R = NMe_2	*o, m*	**20**
	p	**85**

Table 2. Conjugated dienes and trienes (in ethanol); λ_{max} for $\pi \rightarrow \pi^*$ transitions; ϵ_{max} 6000–35 000 ($\times 10^{-2}$ m^2 mol^{-1})

acyclic and heteroannular dienes	215 nm
homoannular dienes	253 nm
acyclic trienes	245 nm
Addition for each substituent	
—R alkyl (including part of a carbocyclic ring)	5 nm
—OR alkoxy	6 nm
—SR thioether	30 nm
—Cl, —Br	5 nm
—OCOR acyloxy	0 nm
—CH=CH— additional conjugation	30 nm
if one double bond is exocyclic to one ring	5 nm
if exocyclic to two rings simultaneously	10 nm
solvent shifts minimal	

Table 3 αβ-Unsaturated carbonyl compounds (in ethanol); λ_{max} for $\pi \rightarrow \pi^*$ transitions; ϵ_{max} 4500–20 000 ($\times 10^{-2}\ m^2\ mol^{-1}$)

ketones —C(β)=C(α)—CO— acyclic or 6-ring cyclic	215 nm
5-ring cyclic	202 nm
aldehydes —C=C—CHO	207 nm
acids and esters —C=C—CO_2H(R)	197 nm

Additional conjugation

—C(δ)=C(γ)—C(β)=C(α)—CO— etc. add 30 nm

(If the second double bond is homoannular with the first, add 39 nm)

Addition for each substituent

	α	β	γ	δ
—R alkyl (including part of a carbocyclic ring)	10 nm	12 nm	17 nm	17 nm
—OR alkoxy	35 nm	30 nm	17 nm	31 nm
—OH hydroxy	35 nm	30 nm	30 nm	50 nm
—SR thioether	—	80 nm	—	—
—Cl chloro	15 nm	12 nm	12 nm	12 nm
—Br bromo	25 nm	30 nm	25 nm	25 nm
—OCOR acyloxy	6 nm	6 nm	6 nm	6 nm
—NH_2, —NHR, —NR_2 amino	—	95 nm	—	—
if one double bond is exocyclic to one ring		5 nm		
If exocyclic to two rings simultaneously		10 nm		

Solvent shifts (see section 4.4)

Above values shifted to longer wavelength in water, and to shorter wavelength in 'less polar' solvents. For common solvents the following corrections should be applied in computing λ_{max}

water	+8 nm
methanol	0
chloroform	−1 nm
dioxan	−5 nm
diethyl ether	−7 nm
hexane	−11 nm
cyclohexane	−11 nm

Double bond endocyclic in 5 - or 7 - membered ring except cyclopent-2-enone - +5 nm

Table 4.1 Approximate Proton Chemical Shifts

Type of proton	Chemical shift, δ, ppm
1° Alkyl, RCH_3	0.8 – 1.0
2° Alkyl, RCH_2R	1.2 – 1.4
3° Alkyl, R_3CHR_2	1.4 – 1.7
Allylic, $R_2C{=}\underset{\displaystyle R}{\underset{\vert}{C}}{-}CH_3$	1.6 – 1.9
Benzylic, $ArCH_3$	2.2 – 2.5
Alkyl chloride, RCH_2Cl	3.6 – 3.8
Alkyl bromide, RCH_2Br	3.4 – 3.6
Alkyl iodide, RCH_2I	3.1 – 3.3
Ether, $ROCH_2R$	3.3 – 3.9
Alcohol, $HOCH_2R$	3.3 – 4.0
Ketone, $R\underset{\displaystyle O}{\underset{\Vert}{C}}CH_3$	2.1 – 2.6
Aldehyde, $R\underset{\displaystyle O}{\underset{\Vert}{C}}H$	9.5 – 9.6
Vinylic, $R_2C{=}CH_2$	4.6 – 5.0
Vinylic, $R_2C{=}\underset{\displaystyle R}{\underset{\vert}{C}}H$	5.2 – 5.7
Aromatic, ArH	6.0 – 9.5
Acetylenic, $RC{\equiv}CH$	2.5 – 3.1
Alcohol hydroxyl, ROH	0.5 – 6.0‡
Carboxylic, $R\underset{\displaystyle O}{\underset{\Vert}{C}}OH$	10 – 13‡
Phenolic, ArOH	4.5 – 7.7‡
Amino, $R{-}NH_2$	1.0 – 5.0‡

‡The chemical shifts of these groups vary in different solvents and with temperature and concentration.

Table 4.2 Approximate Carbon-13 Chemical Shifts.

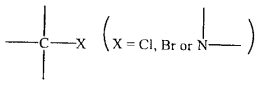
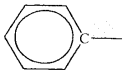
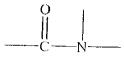
Type of carbon	Chemical shift, δ, ppm
1° Alkyl, RCH_3	0 – 40
2° Alkyl, RCH_2R	10 - 50
3° Alkyl, R_3CHR_2	15 – 50
Alkyl halide	
or amine, 	10 – 65
Alcohol or ether, 	50 – 90
Alkyne, –C≡	60 – 90
Alkene, 	100 - 170
Aryl, 	100 – 170
Nitriles, –C≡N	120 – 130
Amides, 	150 – 180
carboxylic acids, esters, 	160 – 185
Aldehydes, ketones, 	182 – 215

CHART 1. The Carbon Skeleton

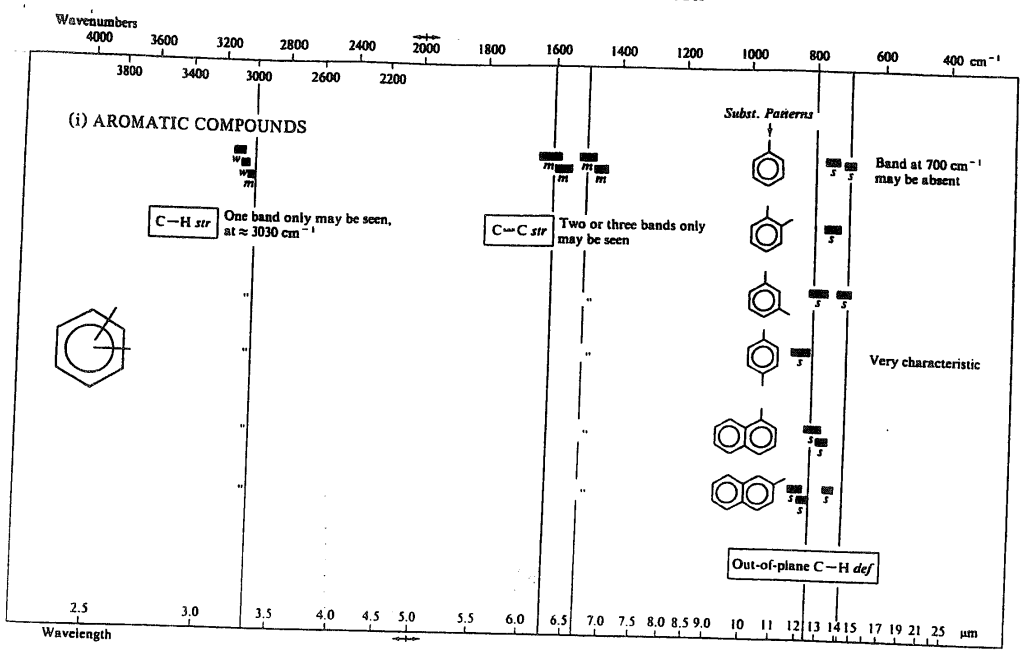


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CHART 1. The Carbon Skeleton (*cont'd*)

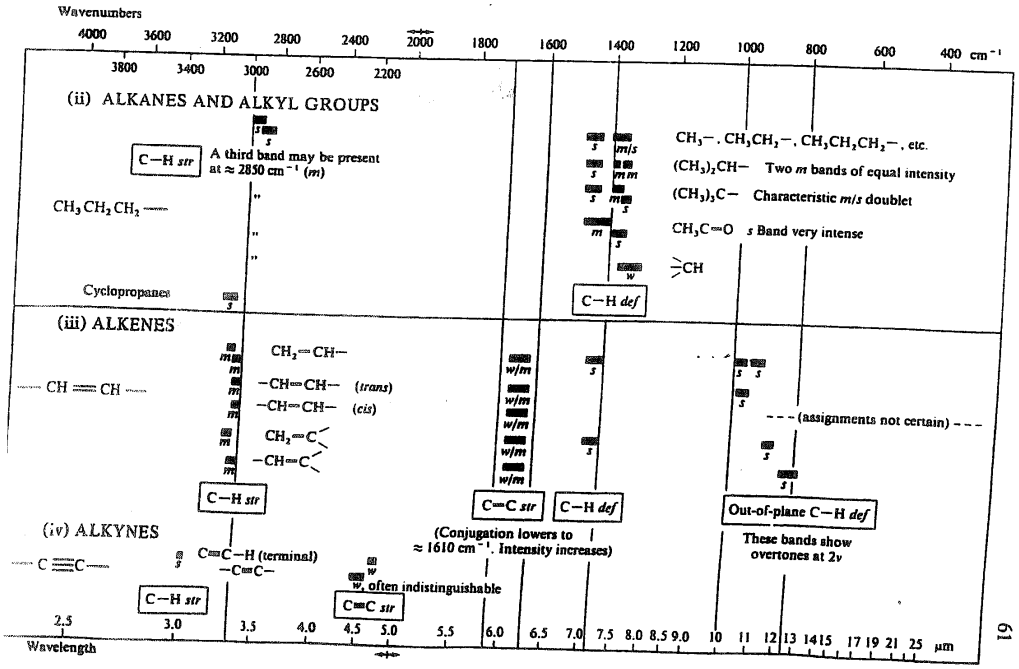

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CHART 2. Carbonyl Compounds

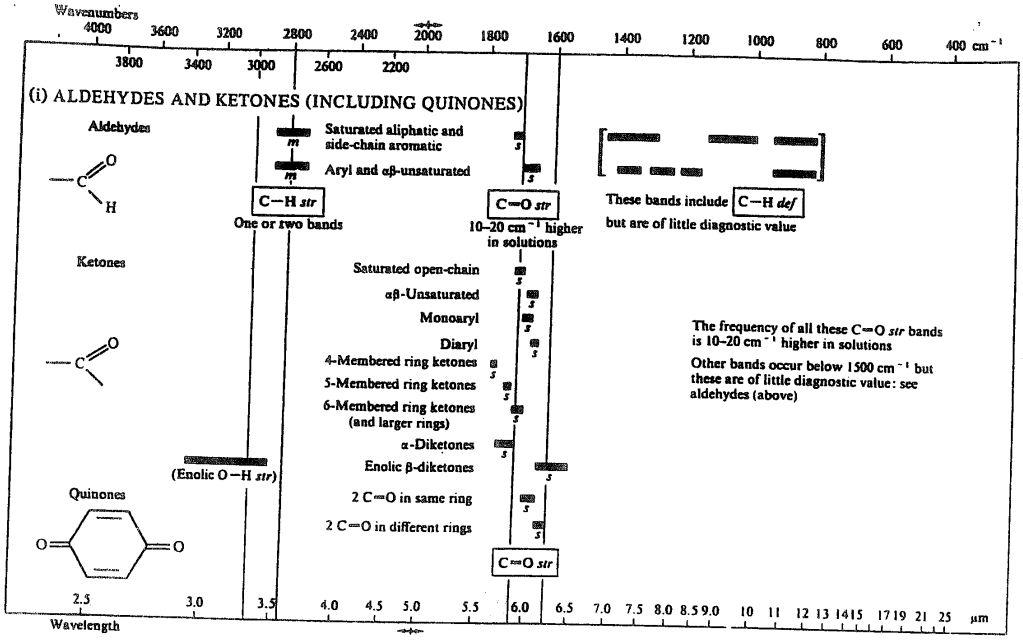

CHART 2. Carbonyl Compounds (*cont'd*)

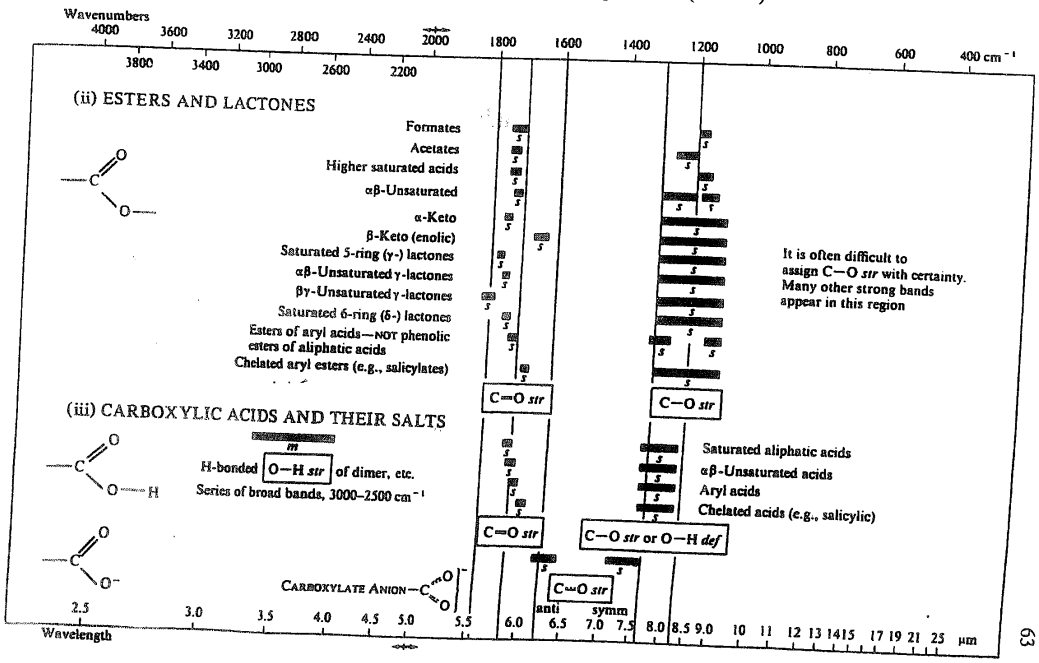

CHART 2. Carbonyl Compounds (*cont'd*)

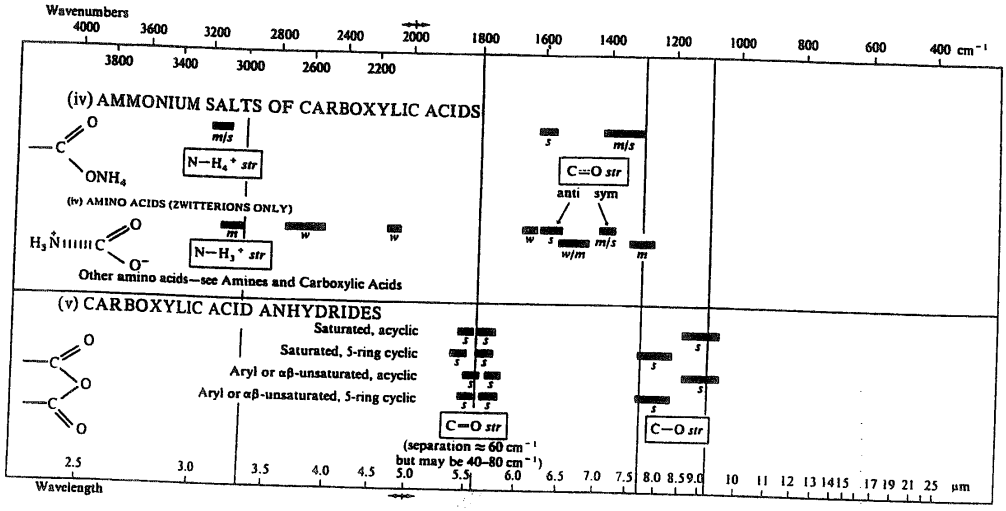

CHART 2. Carbonyl Compounds (*cont'd*)

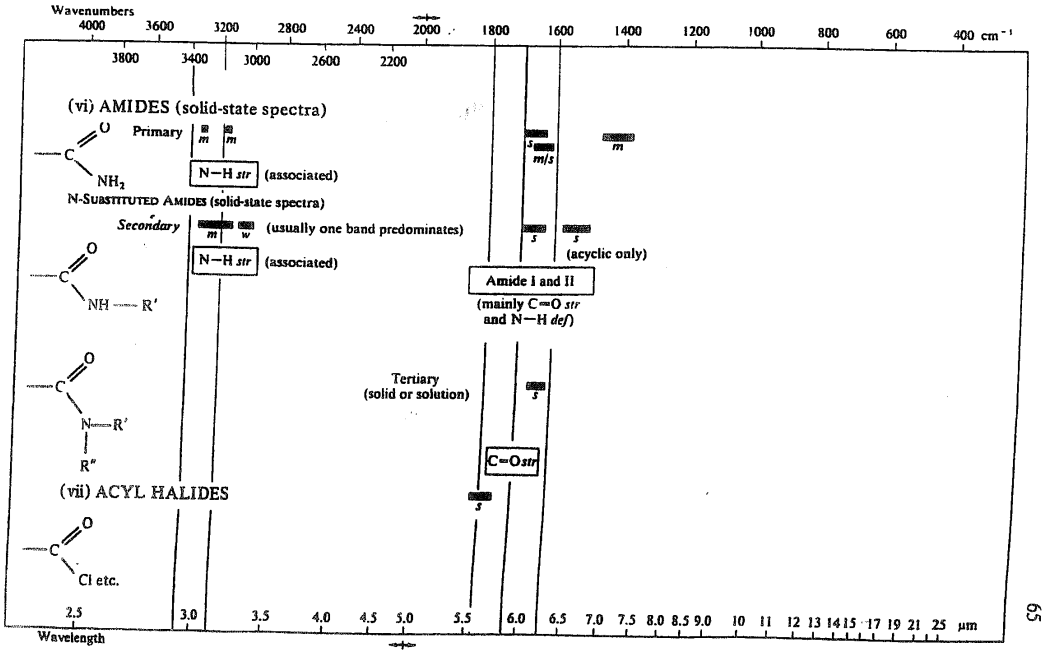

CHART 3. Hydroxy Compounds and Ethers

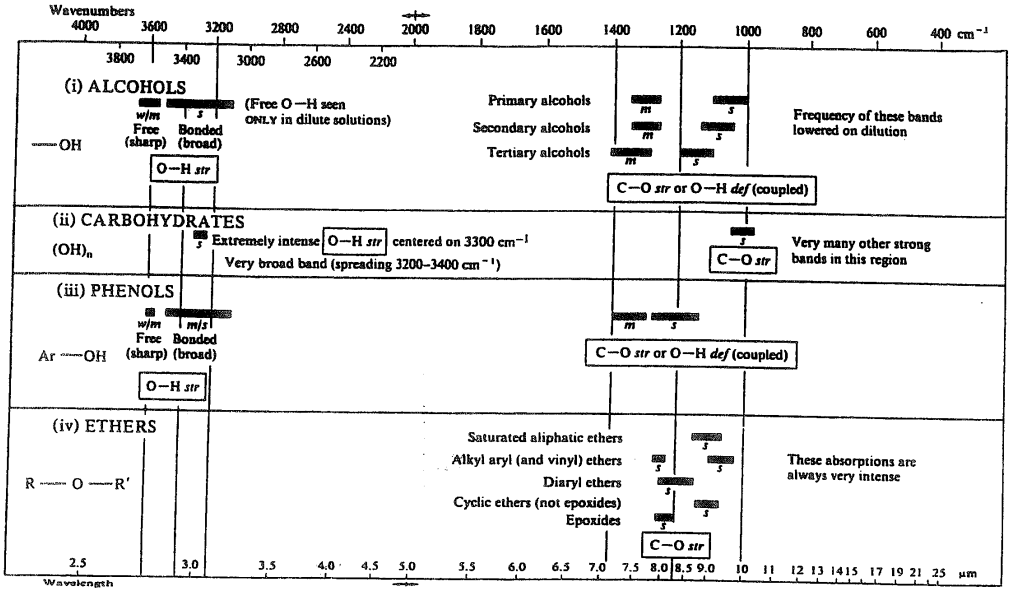

CHART 4. Nitrogen Compounds

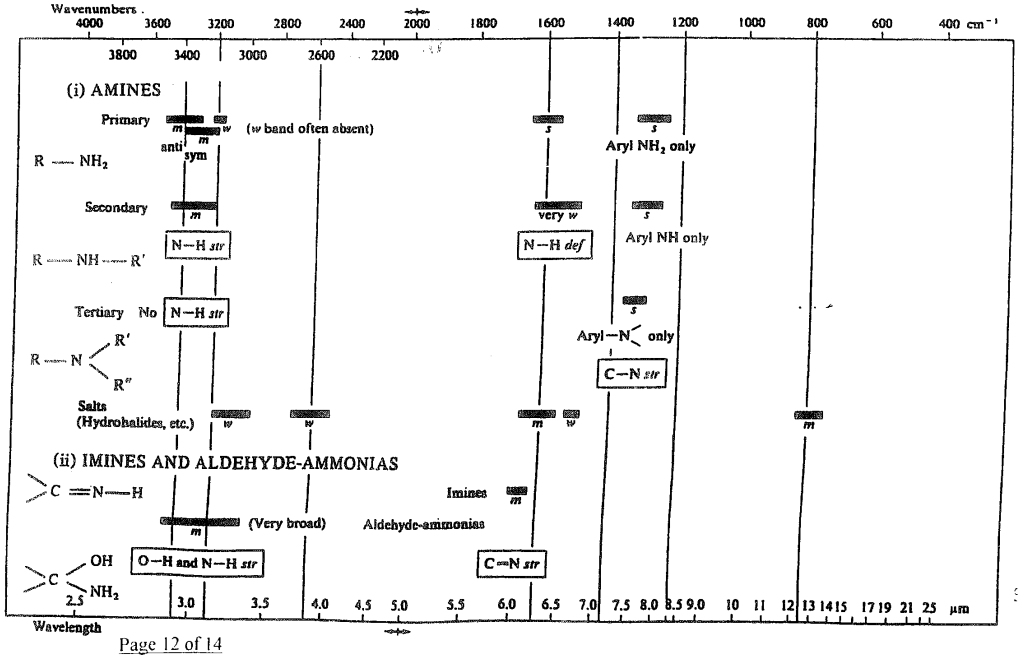

CHART 4. Nitrogen Compounds (*cont'd*)

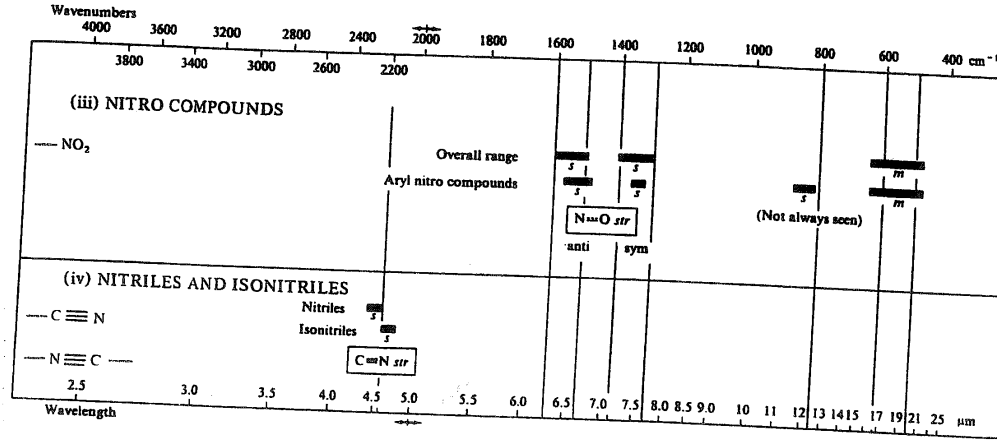

CHART 5. Halogen Compounds

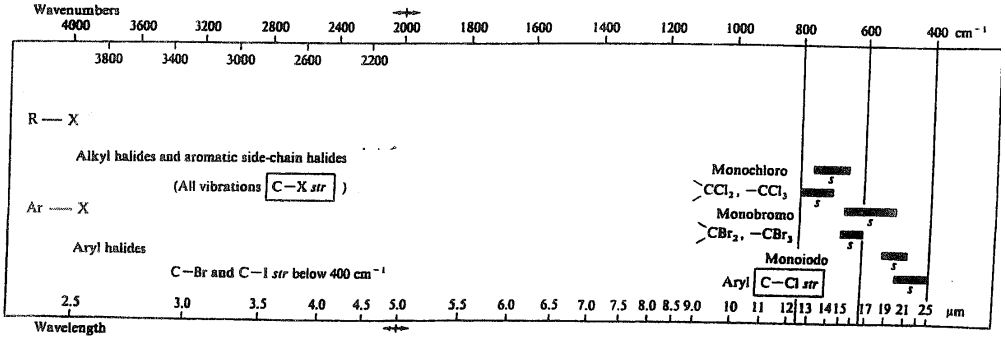

CHART 6. Sulfur and Phosphorus Compounds

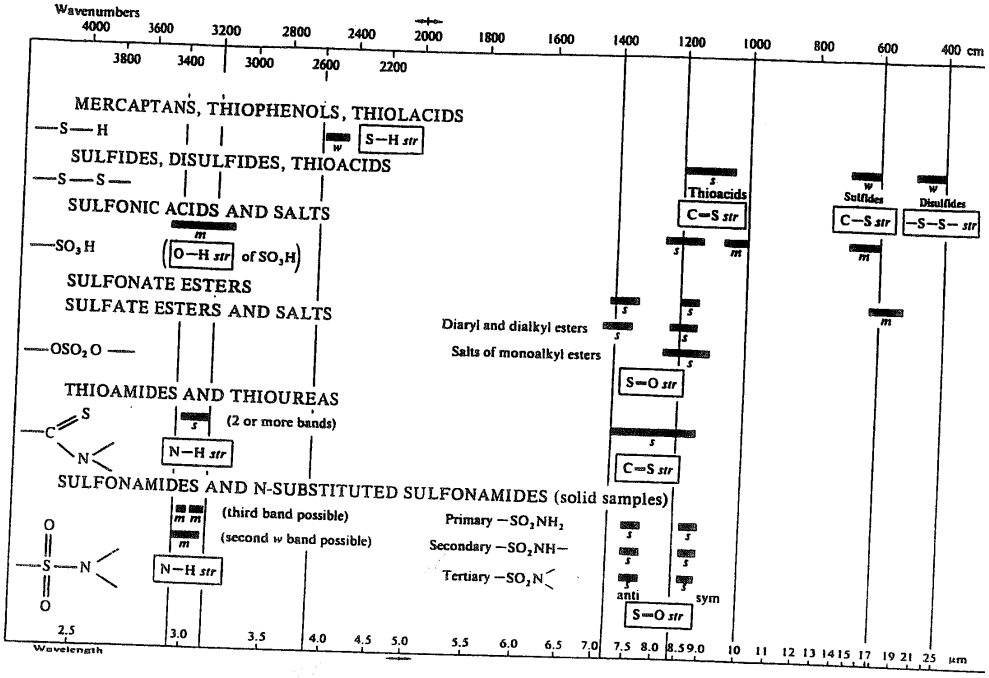

CHART 6. Sulfur and Phosphorus Compounds (*cont'd*)