University Questions

D-52716 - JAN-2014

① calculate λ_{max} in UV of the compds shown below
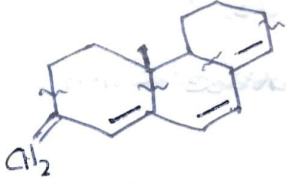
Heteroanular conj·diene = 215 nm

ring residue = 4×5 = 20

double bond extending conjugation = 2×30 = 60

exocyclic double bond = 5 = 300 nm·
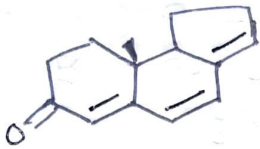
② predict the δ values in ppm of the methyl groups in the ^{13}C NMR Spectra of

CH_2-CH_3 (27 ppm)

OCH_3 (δ- 54 ppm)
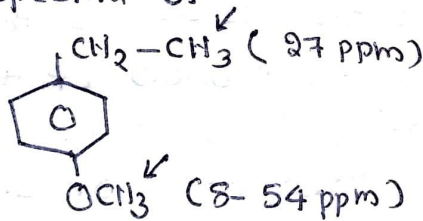
? ③ Give distinction by IR : $Ph-\overset{\overset{O}{\|}}{C}-\ddot{O}CH_3$ and $CH_3-\overset{\overset{O}{\|}}{C}-\ddot{O}-Ph$

1724   I   1765   II

Esters have $\nu_{C=O}$ stretch $= 1750-1735$ cm^{-1}

ν_{C-O} Stretch $= \sim 1250$ cm^{-1}

wave no of absorption is higher than ketones due to −I effect of extra oxygen. when conjugation increases $\nu_{C=O}$ decrease to lower wave number. Conjugation effect is higher in First case (electron release from oxygen) than II. So I will have lower $\nu_{C=O}$ than II ·

④ $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ and $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ by Mass

Gives diff m/z values.

⑤ Explain what is Circular Dichorism and mention its use?

⑥ Explain the ① increase in the $\nu_{C=O}$ stretch frequency in cm^{-1} of cyclic aliphatic ketones as the ring size decreases.

② high abundance of a peak at m/z 91 in the electron impact mass spectra of benzylic compounds?

①
→ C=O stretch frequencies in cycloalkanones increase with decrease in the ring size   (Ref: Jag Mohan)

$\nu_{C=O}$ cm^{-1}			
1717	1717	1745	1780	1828 cm^{-1}
Strain - 0°		0.75°	9.75°	24.25°
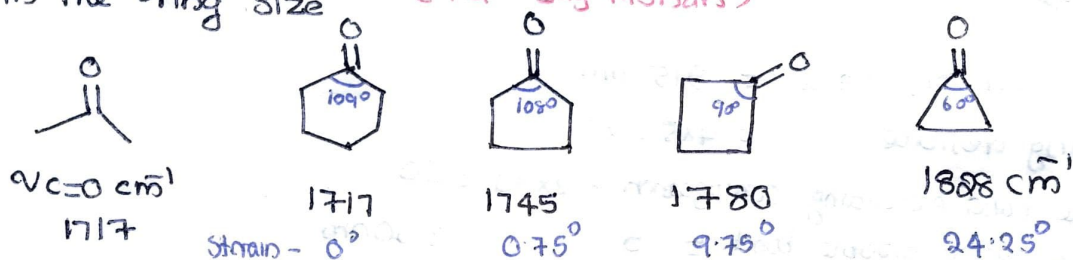
In compounds with rings smaller than n=6 the angle ⊙ is less than normal tetrahedral angle (109.5°) thus causing strain which alters the carbonyl stretching frequency.

$$ ⊙ \propto \frac{1}{\nu_{C=O}} $$

the increase in the carbonyl absorptions as the ring size decreases (angle ⊙ decreases) is due to the increased interaction b/w the carbonyl double bond and the associated neighbouring single bonds. This increased interaction as the ring size decreases, offers resistance to the motion of the carbonyl carbon during stretching vibration, thus increasing its force constant and consequently the frequency of absorption. Highly strained bridged ketones have relatively higher $\nu_{C=O}$ value 1800 cm^{-1}
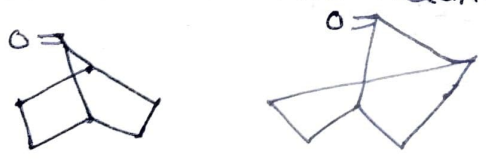
②
→ due to the formation of resonance stabilized benzylium cation ($m/z = 91$) (tropylium cation)

⑦ p-MeO C$_6$H$_4$ CH$_3$ Shows in its ^{1}H NMR spectrum two peaks at δ 2·34, S, 3H and δ 3·75, S, 3H. Assign these two signals? How can an aldehyde distinguished from ketones by NMR and IR.

CH_3 (2.34)

OCH_3 (3.75)
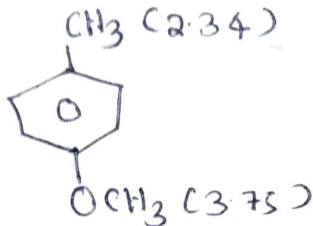
→ aldehydes absorbs at higher wave number than ketones. alkyl group having +I effect decreases the bond strength, hence the force constant and wave no of absorption
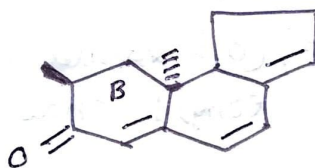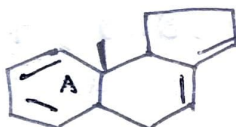
CH_3CHO (1745 cm^{-1}) $CH_3-CO-CH_3$ (1715 cm^{-1})

⑧ Explain the use of ORD for determining the conformation and configuration of 3-alkyl cyclohexan-1-ones.?

⑨ Explain the use of 'H NMR spectroscopy in the structure elucidation of organic compds ? Calculation of λmax of dienes and dienones ? octant rule ? simplification of complex NMR ?

⑩

C 98436 - July 2012

① predict λmax

② compds with primary amino group show neat IR spectra with two bands due to N-H bonds. why and how do these originate?

Ref: Jag Mohan.

Dilute solutions of 1° amines in non polar solvents exhibit two N-H stretching vibrations, one near 3550-3300 cm^{-1} due to N-H asymmetric stretching and the other near 3450-3250 cm^{-1} due to N-H symmetric stretching vibration. 2° amines display one N-H stretch vib from 3500-3300 cm^{-1}, 3° amines do not show any N-H stretching vibration.

Liquid primary amines exhibit medium to strong N-H in plane bending vibration near 1650-1580 cm^{-1}.

③ Explain the axial haloketone rule ? what is its application?

④ Explain the principle of characteristic group frequency based on which IR Spectroscopy is useful in identifying

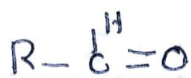functional groups. How can nitrile, nitro and aldehyde group is identified by IR?

$R-C\equiv N$ $\nu_{C\equiv N} - 2280-2200\ cm^{-1}$

$R-N\equiv C$ $\nu_{N-C} - 2275-2250\ cm^{-1}$

$R-NO_2$ — Nitro group has two identical NO bonds which vibrate asymmetrically causing strong absorption near $1565-1515\ cm^{-1}$ and symmetrically near $1385-1335\ cm^{-1}$

$R-\overset{H}{\underset{}{C}}=O$ $\nu_{C=O} = 1740\ cm^{-1}$

⑤ What are the use of metastable peaks in EI Mass Spectroscopy? How do these arise?

⑥ Discuss the use of δ values and J values in deriving structural information from NMR spectra for the structure determination of organic compds?

⑦ Find the structure of a compound $C_7H_7NO_2$ which shows   IR: 3005, 2870, 1605, 1550, 1355, 805 cm^{-1} NMR: δ (2.5, S, 3H) (7.2, doublet of doublet, 2H) (8.2, doublet of doublet, 2H), 7.05, d, 2H upon reduction it forms a compd that dissolve in dil acid?
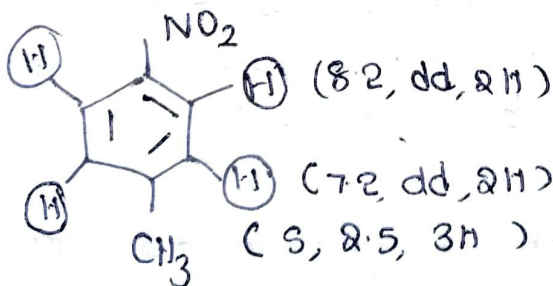
DBE

$C_x H_y N_z$
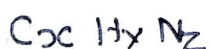
$$DBE = (x+1) - \left(\frac{y-z}{2}\right)$$

O, S — can be ignored.

$$C_7 H_7 NO_2 = (7+1) - \left(\frac{7-1}{2}\right) = 8-3 = 4,\quad \begin{array}{l}3\ double\ bond\ +\\ one\ ring\end{array}$$

H (8.2, dd, 2H)

H (7.2, dd, 2H)

CH₃ (S, 2.5, 3h) on Red^n converts to amine - which is soluble in acid.

IR

3005 — aromatic C-H Stretch vibration

2870 — C-H stretch of CH₃ $\nu_{sym} - 2840$, $\nu_{asym} - 2920$

1605 — C=C aromatic

Ref - Jag Mohan.
PNO - 65

1580 — asymmetric ν_{N-O} strel

1355 — Symmetric ν_{N-O} str

805 — C-H out of plane bending vibration of p-disubstitued benzene ring

D-31623 — December 2012

① which IR bands would help to identify compounds with

(a) nitrile   b) phenyl group.

$\nu_{C \equiv N}$ — 2280-2200 cm^{-1}

aromatic C-H strele 3100-3000 cm^{-1}

$\nu_{C=C}$ stretch = 1600-1580 cm^{-1}

C-H in plane bending — 1300-1000 cm^{-1}

C-H out of plane — 900-667 cm^{-1}

② Esters show higher $\nu_{C=O}$ stretch band compared to ketones why?

R-$\overset{O}{\overset{||}{C}}$-R , R-$\overset{O}{\overset{||}{C}}$-O-R
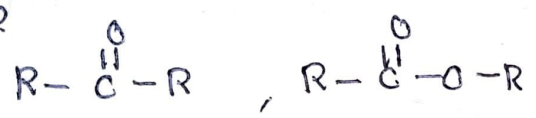
Due to extra oxygen there is −I effect, which strengthens C=O bond, K ↑so ν_{abs} increases.

③ what are Cotton curves? Explain their use in structure determination?

④ write brief notes on (i) ^{13}C NMR spectroscopy (ii) metastable peaks "in Mass Spectra,

⑤ Explain how the coupling constant values help in obtaining Stereochemical information from ¹HNMR Spectroscopy?

⑥ Discuss @ McLafferty rearrangement b) Retro Diels Alder Fission in mass Spectroscopy? Effect of Structural factors on $\nu_{C=O}$ in IR?

⑦ A compound with the molecular composition C_7H_6O shows in its ¹H NMR spectrum peaks at δ: 9.8, δ, 1H, 7.2, S, 5H. It reacted with hydroxylamine and the

product so obtained was reacted next with P_2O_5 &24 to obtain another compd C_7H_5N which showed peak at ~221 in its IR and a singlet at δ 7.3, s, 5H in its 1H NMR Spectrum. what are these two compounds?
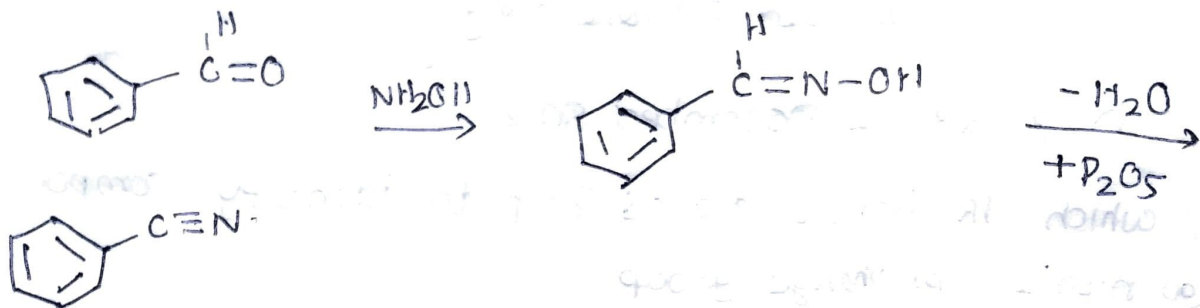
9186   November
D-6894 , June - 2010

① which characteristic functional group in a nitrogen containing compd would show in its IR Spectrum a sharp peak in the region 2200 cm⁻¹. Explain?

C≡N

② write an account of ORD and its use in Structure deter. mination.

③ what are ① ortho effect ② retro D.A fission in EI Mass Spectroscopy?

④ explain use of shift reagent in NMR Spectroscopy.

D-1703, November 2009

① A nitrogen containing aromatic compd shows strong bands at 1550 and 1350 cm⁻¹. identify the functional group present in it?
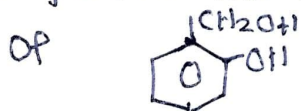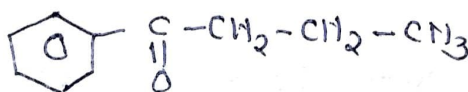

ν_{N-O} (asym) = 1550 cm⁻¹
ν_{N-O} (sym) = 1350 cm⁻¹
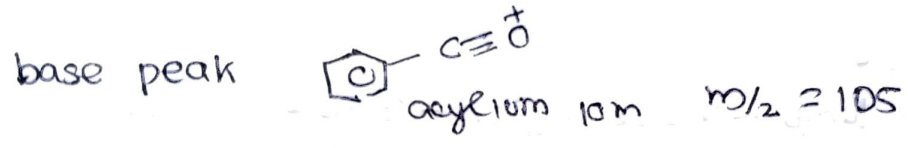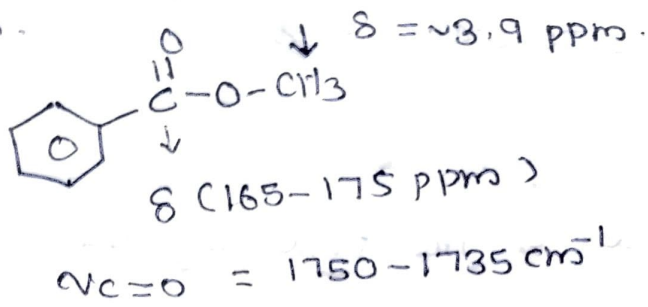
② predict the major peaks you expect in the EI mass spectrum of

 and

③ identify of ketone functionality by IR and ¹³C NMR.

④ explain the use of high field strength in the order of ^1H NMR spectra?

⑤ Consider the structure of methyl benzoate and predict the (1) δ value of its methyl H^3 in ^1H NMR (2) δ value of Carbonyl carbon in ^{13}C. (3) $\nu_{C=O}$ in IR (4) base peak in EI Mass spectra.

↓ $\delta = \sim 3.9$ ppm.

δ (165-175 ppm)

$\nu_{C=O} = 1750-1735 \, cm^{-1}$

base peak

acylium ion $m/z = 105$

⑥ identify the structure

Mol formula — $C_8 H_{10} O_2$

IR − 3000, 2951, 2936, 1509, 1464, 1233, 1060, 827

^1H NMR − δ 3.75, S, 6H , δ 83.5, 4H

^{13}C NMR (off resonance splitting in parenthesis) − 56 (q), 114 (d), 153 (S), , EI − 138 (base peak), 123, 95, 41.

Heating with Hydroiodic acid gave CH_3I and an alkali soluble compound.

$C_8 H_{10} O_2$

$DBE = 8+1 - \dfrac{10}{2} = 9-5 = 4$ → Aromatic ring

^1H NMR −

^{13}C NMR
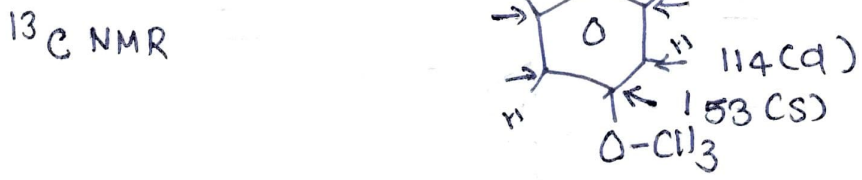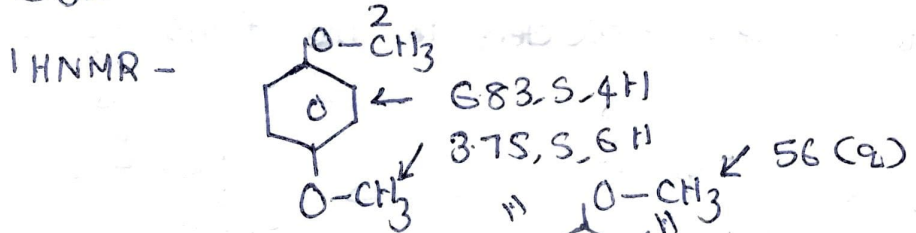
IR —   3000 — Arom C-H Stretch
       2951 — CH_3 asymmetric stretch
       2936 — CH_3 Symmetric stretch
       1233 —   C-O-C Stretch (asym)
       1060.   C-O-C   "   (sym)
       827   — C-H out of plane bending
       1509,1464 — C=C stretch - ph

D-1344, November 2009

① What are the sources of the following radiations   10
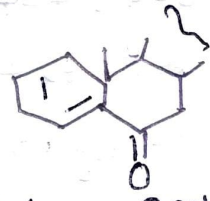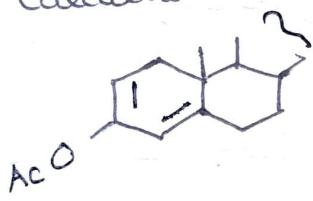Spectrometers ?

   (a) UV   (b) Visible
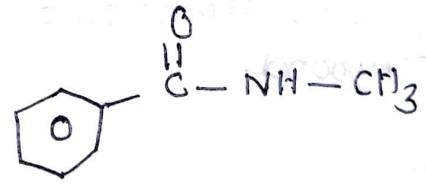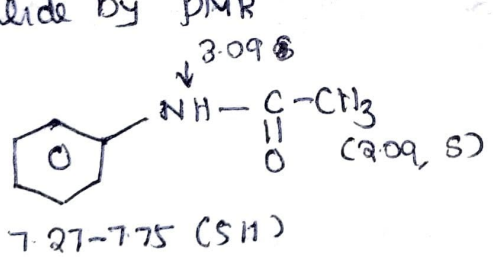   Tungsten filament lamp — visible region - 350-800 nm
   H or D discharge tube —   UV region   — 185-390 nm.

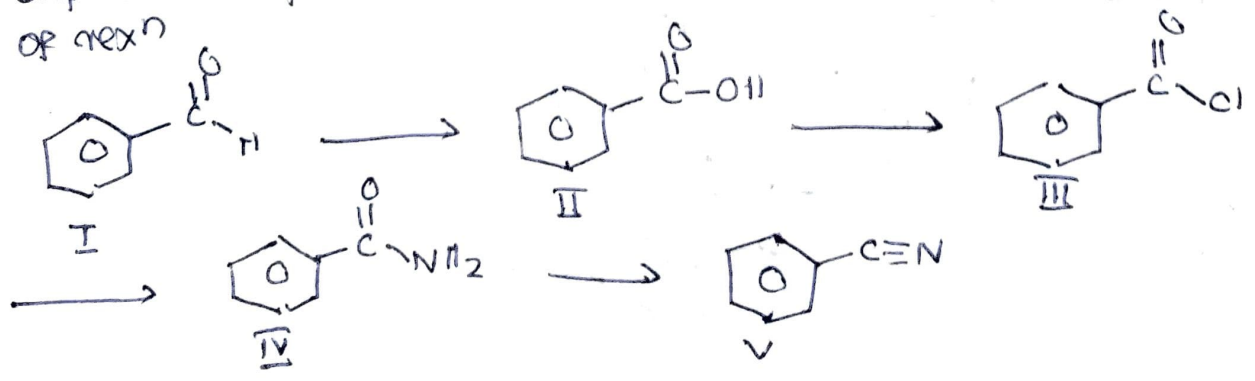② Give distinction of Chromophore and auxochrome with examples?

③   Calculate λmax ?

   AcO

④ How do you distinguish b/wn acetanilide and N-methye ben-
   zanilide by PMR

   7.27-7.75 (5H)

⑤ Explain IR spectral changes expected in the following Sequence
   of rexn

25. I $\nu_{C=O}$ = $1740 - 1690$ cm^{-1}

aldehyde ν_{C-H} (streleh) = $2830 - 2695$ cm^{-1}

II ν_{O-H} - 3000 cm^{-1} (broad)

acids $\nu_{C=O}$ = ~ 1760 cm^{-1} (monomeric)

= $1720-1680$ (dimeric due to H bonding)

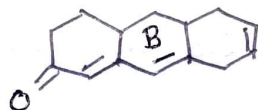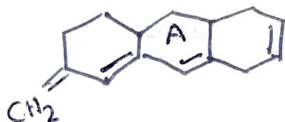III $\nu_{C=O}$ = $1870 - 1770$ cm^{-1} due to high EN of Cl

acid halide

IV

amide ν_{N-H} (free) - $3500 - 3400$ cm^{-1}

(H bonded) - $3350 - 3180$ cm^{-1}

$\nu_{C=O}$ - $1690 - 1670$ cm^{-1}

Nitrile $\nu_{C≡N}$ - $2280 - 2200$ cm^{-1}

D-52718, January 2009

① Which one have higher λ_{max} ?

② Suggest the number of the distinct peak that you would expect in the ^{13}C NMR of Toluene, O-xylene, m-Xylene and P-Xylene.
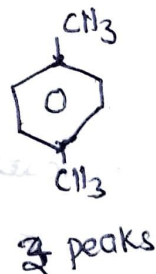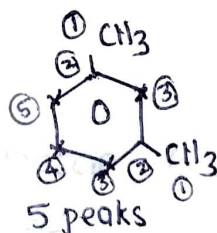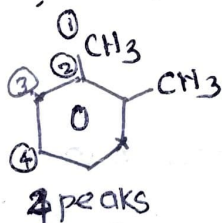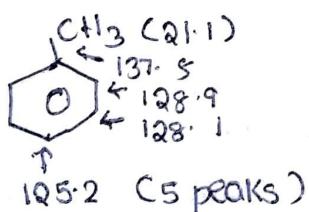
③ Select a suitable spectral method for distinguishing

(1) $MeO-CO-CH=CH_2$ and $CH_2=CH-\overset{O}{\underset{O}{C}}-O-Me$

(2) $p-Me-\overset{O}{C}-C_6H_4-O-CH_3$ and $p-Me-C_6H_4-\overset{O}{C}-O-CH_3$

④ Account

a) the formation of ions at $m/z = 66$ in EIMS of phenol

$m/z = 94$ $-CO$ $m/z = 66$ $-H$ $m/z = 65$

b) The loss of MeOH from M^+ ion of methyl ester of o-toluic acid in its EIMS. (ortho effect)
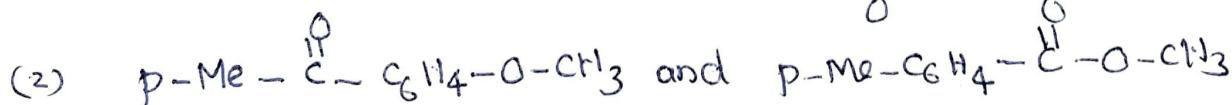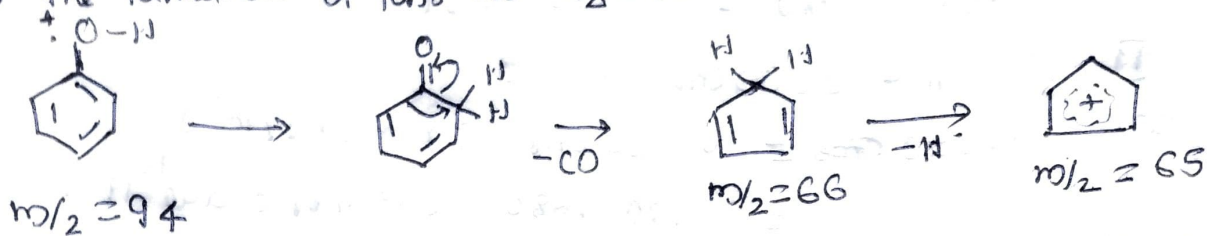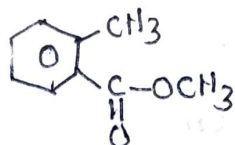

ⓒ The ^1HNMR chemical shift value (in δ) for alkyne hydrogens < alkyne hydrogens < alkene hydrogens

d) $\nu_{C=O}$ stretch value of cyclohexanone is less than that of cyclo pentanone.

⑤ How can chiroptical methods such as ORD be used to study the conformation and configⁿ of 3-methyecyclohexanones?

⑥ Explain ORD curves of cis and trans decalones?

D-41804 - February 2008

① How geometrical isomers can be differentiated by ORD.?

② Indicate which absorption band in the IR spectrum can be used to distinguish b/wn the following pairs of compounds?

(1) $(CH_2)_3N$ and $(CH_3)_2 CH-NH_2$

3°   2°
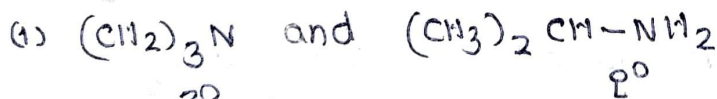
$\nu_{N-H} = No$ band $\nu_{N-H} = 3500-3000 \ cm^{-1}$

CH_3-CH_2-OH $CH_3-\overset{O}{\underset{||}{C}}-OH$
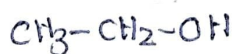
$\nu_{O-H} = 3360 \ cm^{-1}$ (H bonded)

$\nu_{O-H} = 3520$ (free)
$\nu_{O-H} = 3000$ (H bonded)
$\nu_{C=O} = 1760 \ cm^{-1}$

③ How can 2-Methyl butanol and 3-Methyl butanal be distinguished by their mass spectra.

④ write briefly on double resonance technique?

⑤ What is pascals triangle? Explain its use in predicting the PMR Spectrum of the following compound?

$$CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_3.$$

?

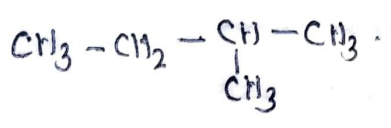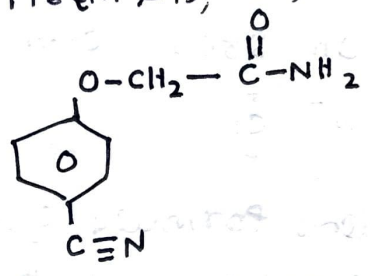⑥ Deduce the structure of the compound having M.P. $C_9H_{18}N_2O_2$. The spectral details as follows.

IR : 3654, 2202, 1683 cm^{-1}

PMR : δ (4·5, s, 2H), (6·0, bs, 2H), (7·1-8·1, m, 4H)

Mass : m/z 176 (m^+ I), 132, 118, 102, 77

132-
118
- 14

⑦ D-88446, Organic Chemistry-III

①

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}C=CH - \underset{\underset{O}{||}}{C} - CH_3 \quad \cdot \text{ Calculate } \lambda_{max}?$$
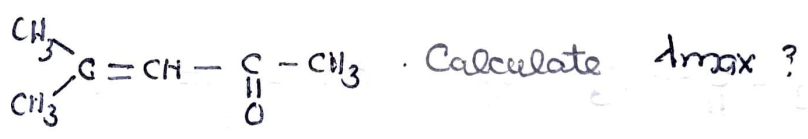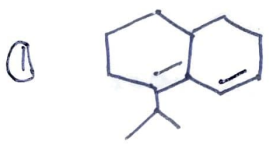
② Explain the splitting pattern expected in the ^1H NMR spectrum of Br- CH =CH₂?
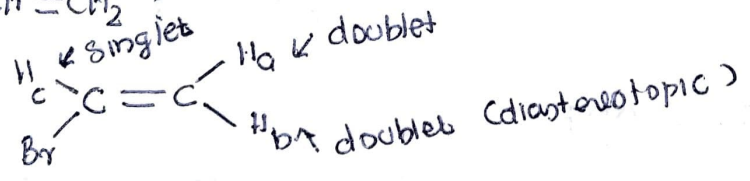
③ Predict the ^{13}C chemical shifts of the following?
(1) $CH_3 - CH = CH- CHO$ (2) $H_3C - O - CH = CH_2$

② $\overset{\frown}{CH_2} = CH - \overset{\frown}{O} - CH_3 \longrightarrow \bar{C}H_2 - CH = \overset{+}{O} - CH_3$

84·2   153·2   55

$$CH_3 - CH = CH \overset{Os}{\underset{\alpha}{C}} - H \longrightarrow CH_3 - \overset{+}{C}H - CH = \underset{\underset{O}{|}}{C} - H \quad 130$$

30.17, 150, 129, 192.2 ppm.

④ An organic compound with M.F $C_3H_5O_2Cl$ exhibits the following spectral data
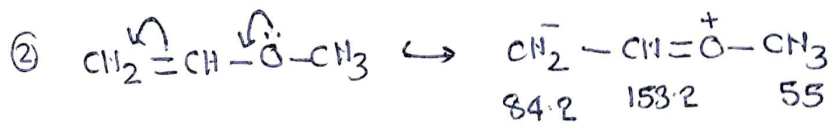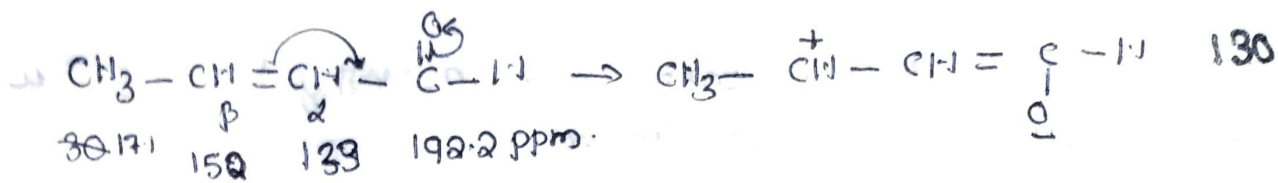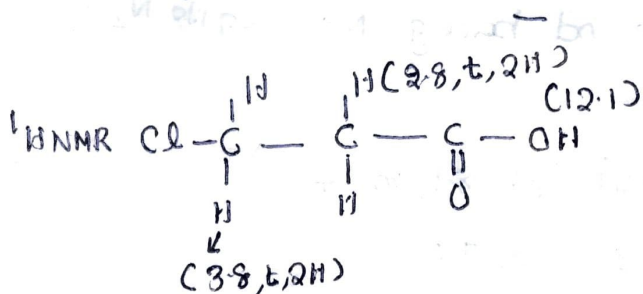
IR : 1710, 2800, 3250 cm^{-1}

NMR: δ 2.8, t, 2H J= 6.9 H2 , 3.8, t, 2H, J = 6.9 H2

10.1, 1H, exchange with D_2O

MS· M$^+$ 108 (3), 110 (1)

^{1}H NMR
$$Cl - \underset{\overset{|}{H}}{\overset{\overset{|}{N}}{C}} - \underset{\overset{|}{H}}{\overset{\overset{H(2.8, t, 2H)}{|}}{C}} - \underset{\overset{||}{O}}{\overset{\overset{H(2.8, t, 2H)}{|}}{C}} - OH \overset{(12.1)}{}$$

(3.8, t, 2H)

IR - 1710 - C=O , 3250 - OH, 2800 - C-H

MS - 108 (M$^+$, ^{35}Cl) , 110 (M$^+$ ^{37}Cl)

⑤ A compound with molecular formula C_3H_6O can exist in two tautomeric forms A and B, which have the following prominent IR absorption bands at (1) 1710 cm^{-1} (2) 3250 cm^{-1}, 1630 cm^{-1}. Give structure for A and B based on the above data.

$$CH_3 - \underset{\overset{||}{O}}{C} - CH_3 \rightleftharpoons CH_3 - \underset{\overset{|}{\underset{H-O}{}}}{C} = CH_2$$

$\nu_{C=O} = 1710$ $\nu_{O-H} = 3250$ cm^{-1} (B)

(A) $\nu_{C=C} = 1630$ cm^{-1}
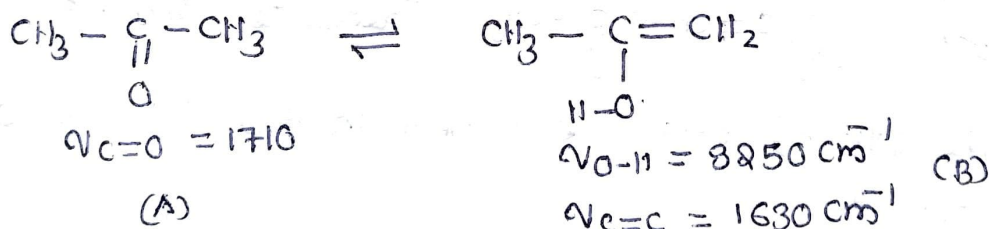
D - 28320 - Feb-2007

① predict the λ_{max} for 3,4,5,6,7,8 - hexahydro-2H-naphthalene-1-one

② In the IR Spectrum of a benzene derivative A ($C_8 H_8 O_2$)
giving a positive hydroxcamic acid test a sharp peak is observed
at 1725 cm⁻¹. predict the possible structure of A
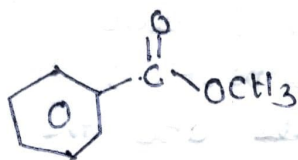
③ Account for the low sensitivity associated with ^{13}C NMR?

④ state and explain nitrogen rule?
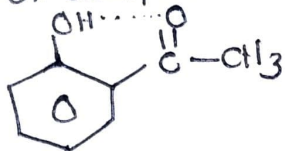
⑤ what is circular birefringence?

⑥ How will you differentiate b/wn o-hydroxy acetophenone and
p-OH acetophenone by IR? and NMR?

The OH group in o-hydroxy compd is involved in intramolecular
hydrogen bonding and hence the value of OH stretching bonded
absorption near 3400-3200 cm⁻¹ remains almost the same is
all dilations, where as OH group in p-hydroxy benz derivative,
is involved in intermolecular H bonding, so will cause low
frequency, broad, intense OH (bonded) absorption to diminish.
And a high frequency sharp rather weak (OH (free)) band of
unbonded hydroxy group to appear.
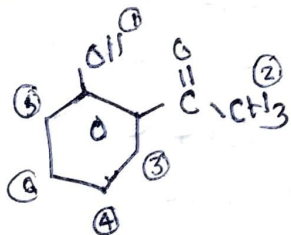
6 signals   4 signals
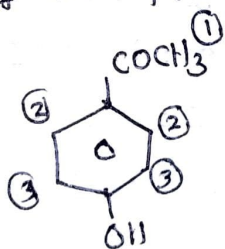
⑦ Differentiate 3-methylcyclohexene and 4-methylcyclohexene by
mass?

by retro DA rxn.

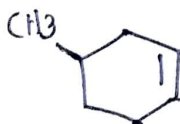⑧ Explain the role of γ-gauche interaction in ¹³C deciding ¹³C chemical shift values?

Unlike α and β effects the γ-effect is negative (-2.5). A γ carbon can have either gauche or anti relationship with the resonating carbon. Moreover the proportion of conformers could differ from molecule to molecule and the value of -2.5 is only an average and is not accurate for all situations and represent only a mix of two conformers. The pure γ anti effect is +1 and the pure γ gauche effect is around -6.

C
Cγ
anti

C
Cγ
gauche
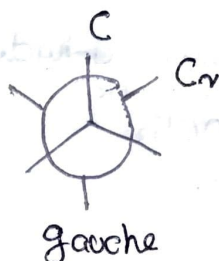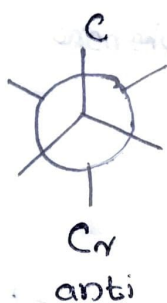
⑨ protons attached to nitrogen appear as broad signal in the ¹H NMR spectrum. Acnt for this observation?

The protons on nitrogen will frequently appear as broad peak due to nuclear quadrapole broadening by N. These protons are exchangable with deuterium.

⑩ Uv (ethanol) = 277 nm (ε = 11600)

IR (neat) = 3050, 2980, 2830, 2735, 1698, 1601, 1515 cm⁻¹

¹HNMR (CDCl₃) = δ 9·6 (s, 1H), 7·5 (d, J=7.5 Hz, 2H₂),
6·7 (d, J=7·5 Hz, 2H₂), 3·6 (s, 3H)

¹³CNMR (CDCl₃) = δ 57·5 (CH₃), 117·2(CH), 131·4 (CH),
132·8 (C), 164·3 (C), 192·4 (C)

MS-(EI) - 136 (M⁺, 56 %), 135 (100 %), 107, 92

Compd gave positive test with Schiffs reagent.

Ans-

H-C=O

O-CH₃

→ ^{1}HNMR

$H - C = O$

896 (H)

(H) (6.7, d, J = 7.5 Hz

(H) (7.5, d, J = 7.5 Hz)

$O-CH_3$ (3.6, 3, 3H)

→ ^{13}C NMR

$O = C - H$ (192.4)

117.2
114

132.8

131.34

164.3

OCH_3
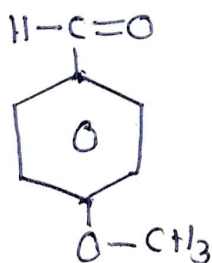
→ MS

136 (M$^+$, 56%)   M$^+$ - H = 135 (100%)
aldihydic CH elimination

$135 - CO (28) = 107$,
$107 - CH_3 (15) = 92$,

→ IR.

→ UV - 277 (n → π*)
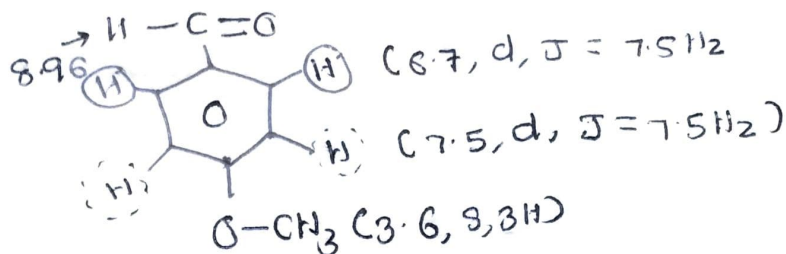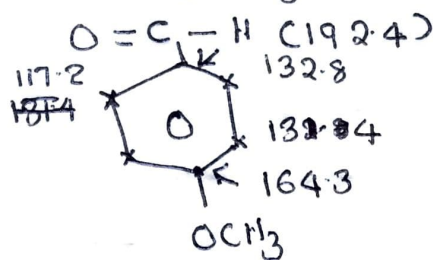
(11) with suitable examples, illustrate the concepts of homotopic enantiotopic and diastereotopic protons. ?

(12) Compare the carbonyl stretching frequency exhibited by cyclobutanone, cyclopentanone and cyclohexanone. Account for the large variation in stretching frequency exhibited by these molecules. ?

(13) in the reaction blwn 1,3-diphenylpropenone and ph MgBr 1,1,3-triphenylprop-2-en-1-ol is formed in satisfactory yield along with an isomeric compound B, that gave a strong peak at 1682 cm^{-1}, in its IR spectrum (1,3-diphenylpropenone gives a peak at 1661 cm^{-1}. when the rexn was repeated in the presence of one equivalent of cupric iodide, B was formed as the only product. Identify B and propose a mechanism for its formation and explain why it is formed exclusively in the presence of cupric iodide ?
(apply HSAB principle)

(14)

① which one will have higher λ_{max} value -
3-methyl-but-3-en-2-one or 3,4-dimethylbut-3-en-2-one.

② Compare the carbonyl stretching frequencies of $RCOCl$ and $RCONH_2$?
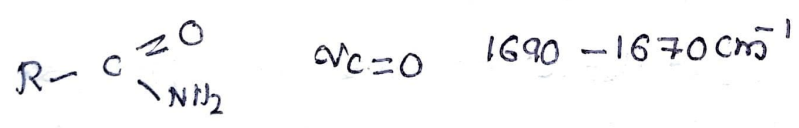
$$R-C \overset{\displaystyle O}{\underset{\displaystyle \ddot{C}l}{\Big\langle}} \longleftrightarrow R-C \overset{\displaystyle \overset{\ominus}{O}}{\underset{\displaystyle \overset{\oplus}{Cl}}{\Big\langle}}$$
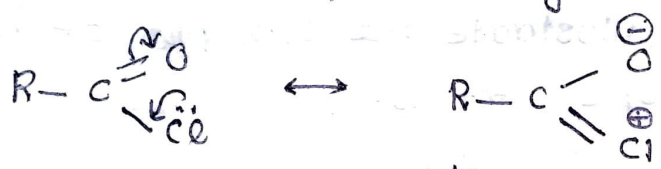
$\nu_{C=O} = 1870$ to $1770\,cm^{-1}$

the high Electronegativity of Cl is the reason for high Stretch freq.

$$R-C \overset{\displaystyle O}{\underset{\displaystyle NH_2}{\diagup}} \qquad \nu_{C=O} \quad 1690 - 1670\,cm^{-1}$$

③ Assign the structure having MF C_5H_{12} exhibits only one ^1HNMR signal?

C_5H_{12} $DBE = 5+1-\dfrac{12}{2} = 6-6 = 0$

So it is aliphatic compd.

$$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} - CH_3$$
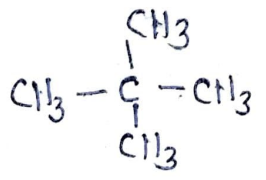
④ predict the ratio of M^+, $(M+2)^+$ and $(M+4)^+$ intensities for CH_2Br_2?

4. $M^+ = 50\% \ (C^{79}Br)$

$(M+2)^+ = 49.5\% \ (^{81}Br)$

$(M+4)^+ = $ Not seen much
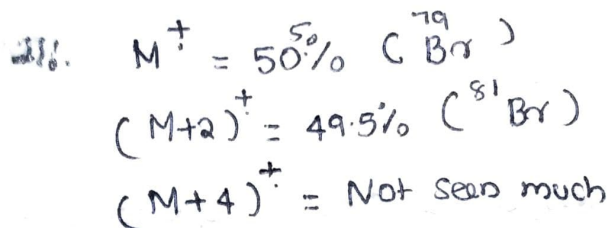
⑤ No geminal coupling is observed in methyl hydrogens of dimethyl ether. why?

$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - O - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - H$$
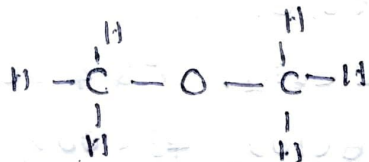
geminal coupling occur only if the protons are non equivalent

⑥ Explain the use of karplus equation in predicting the vicinal coupling constants?

⑦ Three isomeric compounds A, B and C with MF $C_9H_{10}O_2$ have the following IR and PMR data. Identify the compounds?

A   IR $\nu_{C=O} = 1742\,cm^{-1}$

^1H NMR : $7.2\ (5H, S),\ 5.0\ (2H, S),\ 2.1\ (3H, S)$

B   IR $\nu_{C=O} = 1737\,cm^{-1}$

^1H NMR : 7.3 ppm $(5H, S)$ $3.5\ (2H, S)$

            3.6 ppm $(3H, S)$

C   IR $\nu_{C=O} = 1700\,cm^{-1}$

^1H NMR : $10.2\ (1H, S),\ 7.2\ (5H, S)$, Overlapping triplets

                              at 2.9 and 2.8 ppm

$DBE = 9+1-5 = 5$

(A)

$O - \overset{5.0}{CH_2} - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$ (2.1)

phenyl ring 7.2

(B)

$\overset{3.5}{CH_2} - \overset{\overset{\displaystyle O}{\|}}{C} - O - \overset{3.6}{CH_3}$

phenyl ring 7.3 ppm

(C)

$\overset{2.8}{CH_2} - \overset{2.9}{CH_2} - \overset{\overset{\displaystyle O}{\|}}{C} - OH$ (t) 10.2

phenyl ring $\leftarrow 7.2$
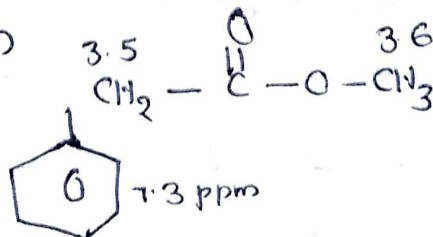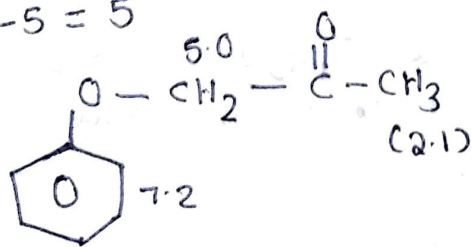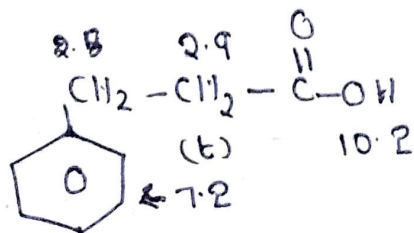
D – 86186   ~~Org~~ Seplember – 2006

① identify the structure of compound whose spectral date

(i) UV (ethanol) – transparent above 220 nm
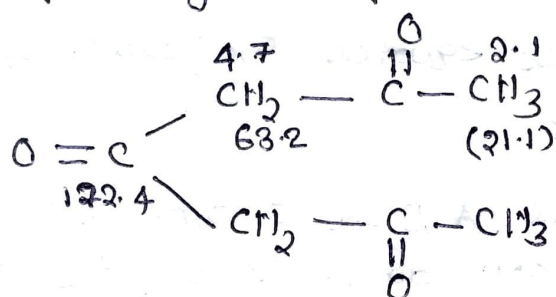
IR (neat) – 2970, 1748 cm^{-1}

^{1}HNMR (CDCl$_3$) – δ 4·7 (S, 4H), 2·1, (S, 6H)

^{13}C NMR (CDCl$_3$) – δ 21·1 (CH$_3$) 63·2 (CH$_2$), 172·4 (C)

MS (EI) – 142 (M$^+$ < 1%), 86 (10), 43 (100),
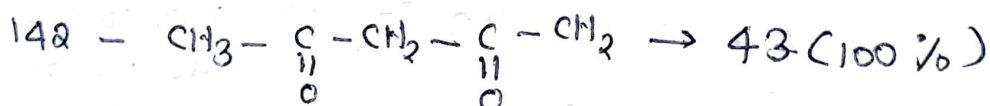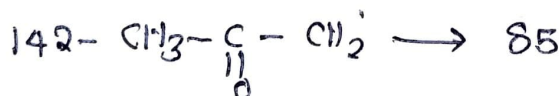
The compound gave a positive iodoform test Cl$_2$ + KOH)

Diacelyl acetone   M.wt – 142

IR → 2970 –   C–H (stretch)

1742 –   C=O

^{1}H NMR

Mass – M$^+$ = 142

142 – CH$_3$–C–CH$_2'$ → 85
          ‖
          O

142 – CH$_3$–C–CH$_2$–C–CH$_2$ → 43 (100%)
          ‖   ‖
          O   O
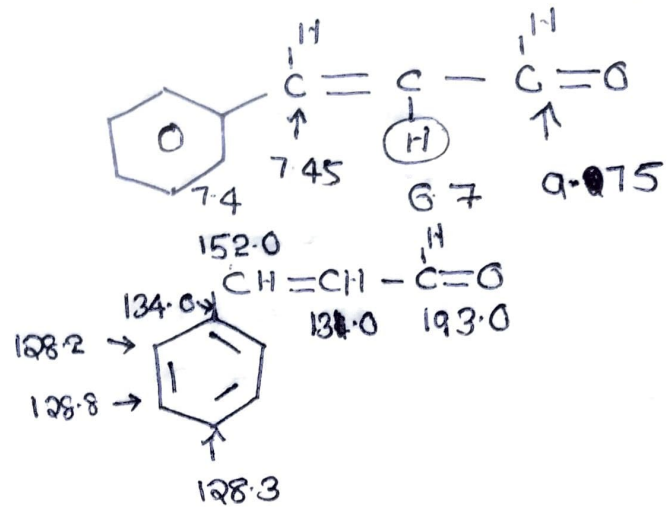
② A compound of mol formula C$_9$H$_8$O exhibits following spectral characteristics. Based on them deduce the structure and stereochemistry of the compol.

(i) V$_{max}$ = 284 and 308 nm

IR = 1690 cm^{-1}

^{1}H NMR = 6·7 (dd, J=16 Hz and 8 Hz, 1H)

7·4 (m, 5H), 7·4 (m, 5H), 7·45 (d, J=16 Hz, 1H

9·75 (d, J = 8 Hz, 1H)

^{13}C NMR — 188.2 (d, 2C), 128.3 (d), 128.8 (d,2C) 139

131.0 (d), 134.0 (s), 152.0 (d), 193.0 (d)
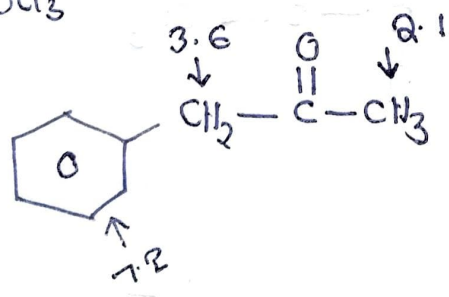
Mass — 132, 131 (base peak), 103.

$\nu_{C=O}$ = 1690

UV — $n \to \pi^*$ transitions

③ A compound of mol formula $C_9H_{10}O$ has the following spectral characteristics. Suggest a suitable structure for the above compd and predict the mass spectral fragmentation pattern.

UV EtOH : λ_{max} 260 nm (305)
285 nm (80)

IR (KBr) : ν 1780 cm^{-1}

^1H (NMR) : δ 2.1 (S, 3H), 3.6 (S, 2H), 7.2 (m, 5H)
CDCl₃

④ How many ^{13}C NMR peaks should be seen in the noise decoupled spectrum of benzyl acetate, n-hexane and p-dichloro benzene. Also assign the multiplicity expected for each signal in

the off resonance decoupled Spectra. what is ^{13} gama gauche140 effect and how is it useful in structural elucidation of ^{13}C NMR.

⑤ A compound whose mass Spectrum showing the molecular ion at m/e 146, has two additional intense peaks at m/z 131 and 103. & IR. −1650 cm^{-1}

^{1}H NMR - 8.3 (s,3H), 6.7 (d, J=16 Hz, 1H), 7.4 (broad m, 5H) 7.5 (d, J=16 Hz, 1H) overlaping with the previous signal. ^{13}C NMR - 8 27 (q), 127 (d), 128 (d,2C), 129 (d,2C), 130 (d) 135 (S), 144 (d), 198 (s). Deduce the structure and stereochemistry ?
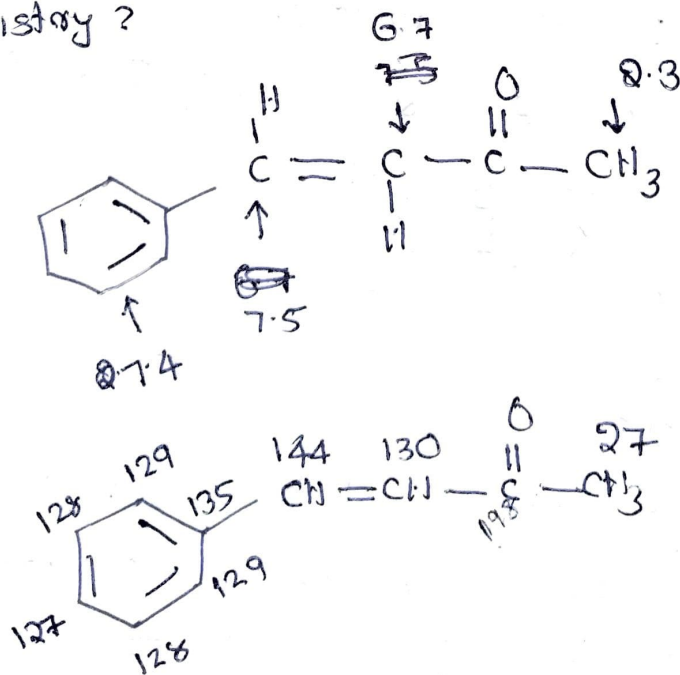
$a_{..}$ $M^+ = 146$, $181 = M^+ - CH_3$, $103 - (M^+ - CH_3)$ 141
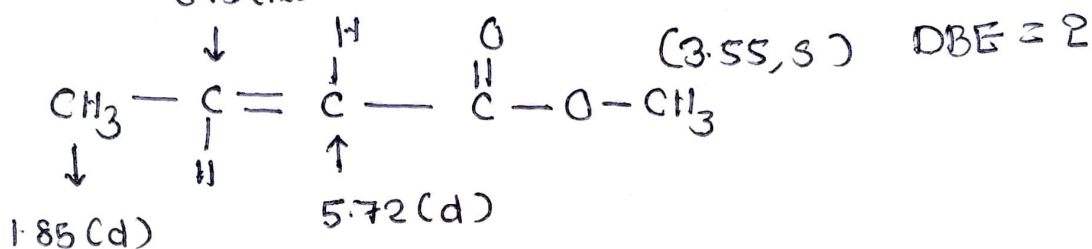 $-CO$

(6)   Mol. formula — $C_5H_8O_2$

IR — No major peaks above 3000,
       1725, 1680, 1600, $980\ cm^{-1}$

^1HNMR — 1.85, d, J = 6 Hz, 3H

              3.55, S, 3H 5.72, d, J = 16 Hz, 1H

              6.75 m, 1H

EIMS — M^+ $100\ (20)$, $85\ (40)$, $69\ (100)$, $59\ (10)$, $41\ (60)$
             $675\ (m)$

$$CH_3 - \underset{\underset{1.85\ (d)}{\downarrow}}{\underset{H}{C}} = \underset{\underset{\uparrow}{\underset{H}{\downarrow}}}{C} - \underset{\underset{5.72\ (d)}{}}{\overset{\overset{O}{\|}}{C}} - O - CH_3 \qquad (3.55, s) \quad DBE = 2$$

$\nu_{C=O} = 1725\ cm^{-1}$ $\nu_{C=C} = 1680\ cm^{-1}$

$M^+ = 100$

$69 = M^+ - \cancel{51} OOCH_3$. $\overset{\overset{O}{\|}}{}$

$41 = M^+ \ominus CH_3 - O - \overset{\overset{O}{\|}}{C}$

$59 = M^{\pm} - CH_3 - CH = CH$

(7) An organic compound of molecular formula $C_{12}H_{17}O_2N$
displays the following spectral characteristics.

    UV = λmax 300 nm (100)

    IR — $1180\ cm^{-1}$ (S), $1630\ cm^{-1}$ (m), $1660\ cm^{-1}$, $1695\ cm^{-1}$ (S)
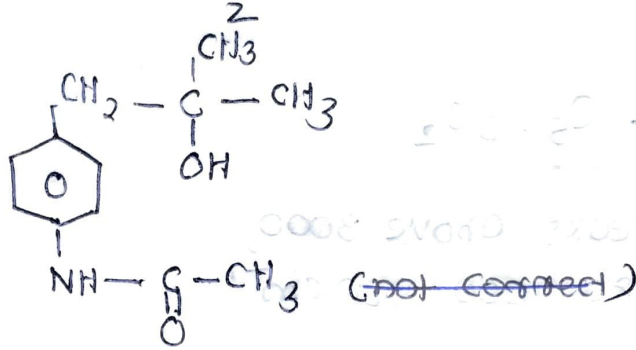 $3500\ cm^{-1}$ (m, double)

    ^1HNMR — 1.5 (S, 6H), 2.8 (S, 2H), 3.6 (S, 3H)
              4.2 (S, 1H, which disappears on D_2O wash) (6.5, bs, 1H)
              $7.6 - 7.8$ (m, 4H),

$$DBE = (12+1) - \frac{(17-1)}{2} = 13 - 8 = 5$$
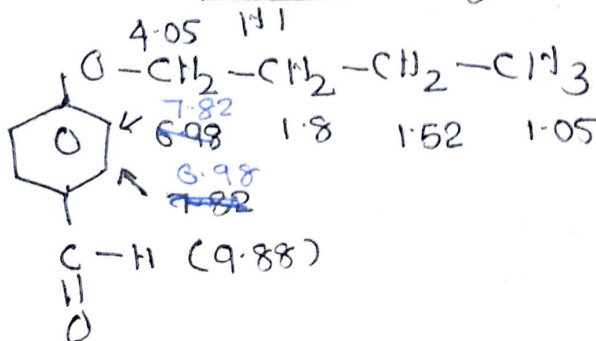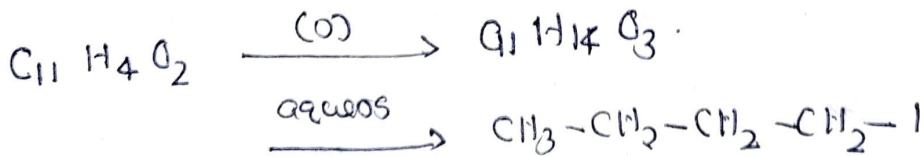
GIVE

$$
\begin{array}{c}
\text{CH}_2-\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}-\text{CH}_3
\end{array}
$$

NH$-\underset{\text{O}}{\overset{\|}{\text{C}}}-CH_3$ (not correct)

⑧ $C_{11}H_{14}O_2$

IR cm^{-1} :   2960,   2900,   2860,   1695,   1605,   1260,   835 cm
                   (C-H)   (aldehyde   (aldehyde   (C=O)   (C=C)   (C-O (asym)   (C-O (sym))
                              (asym))   (sym))   ether

^{1}H NMR (δ):   1.05 (t, 3H),   1.52 (Sextet, 2H),   1.8 (quintet, 2H)
   4.05 (t, 2H),   6.98 (d, 2H),   7.82 (d, 2H),   9.88 (S, 1H)

EIMS   :   M$^+$ -178,   177,   149,   135,   105,   73.

Compd is easily oxidised to an acid $C_{11}H_{14}O_3$. On boiling with aqueous HI, it generates n-butyl iodide.

$$C_{11}H_4O_2 \xrightarrow{\text{(O)}} C_{11}H_{14}O_3$$

$$\xrightarrow[\substack{4.05 \ \text{HI}}]{\text{aqueous}} CH_3-CH_2-CH_2-CH_2-I$$

O$-$CH$_2-$CH$_2-$CH$_2-$CH$_3$
      7.82
   6.98   1.8   1.52   1.05
   6.98
   7.82

C$-$H (9.88)

142

⑨ Compound A shows a M^+ peak at 170 and $[M^+ + 2]$ at
? 172 in the ratio 1:1. Its IR Spectrum has a sharp peak
at 800 cm⁻¹. The ¹HNMR shows a peak at 2.1 (3H, s)
and 6.9 (doublet of doublet, 4H)

$M^+ = 170$, $M+2 = 172$ (1:1)
So there will be ^{79}Br and Br^{81} isotopes.
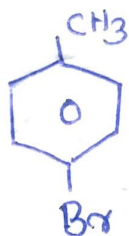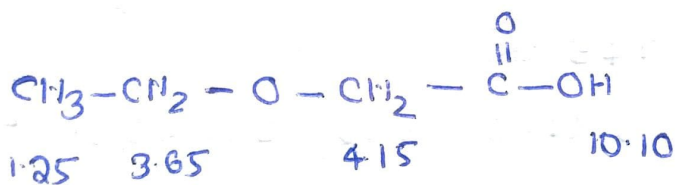

$C_7H_7Br^{79} = 170$

$C_7H_7Br^{81} = 172$

800 cm⁻¹ — C-H out of plane bending vibration of p-disub-
benzene ring.

⑩ UV — 203 nm (40)

IR — 3150 cm⁻¹ (broad), 1718 cm⁻¹ (strong)

Mass — M^+ at 104

¹HNMR — 1.25 (t, 3H), 3.65 (q, 2H), 4.15 (s, 2H), 10.10 (s, 1H)

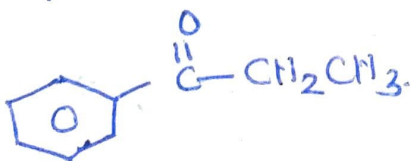$$CH_3-CH_2-O-CH_2-\overset{\overset{O}{\|}}{C}-OH$$
1.25   3.65   4.15   10.10

$C=O$ (1718)   OH (H-bonded) — 3150 cm⁻¹
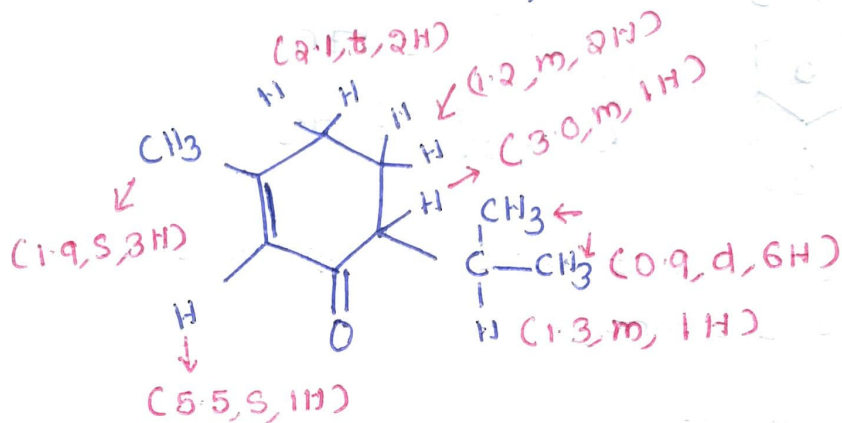
⑩ Mol. formula — ~~C₉H₈O~~

IR = 1600, 1680 cm⁻¹

Mass — 134 (M⁺, 10), 119 (5), 105 (100), 77 (20)

NMR — 8 (10, t, 3H), 2.5 (q, 2H), 7.0 (s, 5H)

⑪ A terpenic compound $C_{10}H_{16}O$ upon reaction with 144 Peroric chloride gave thymol (2-isopropyl-5-methyl phenol). Deduce structure

UV (ethanol) : λ_{max} 237 nm (ε -15,000)

IR : 1700 cm⁻¹

NMR : δ 0.9 (d, 6H), 1.2 (m, 2H), 1.3 (m, 1H)
1.9 (s, 3H), 2.1 (t, 2H), 3.0 (m, 1H)
5.5 (s, 1H)

(2.1, t, 2H)

(1.2, m, 2H)

(3.0, m, 1H)

CH_3
CH_3
CH₃ ←
C—CH₃ (0.9, d, 6H)
H (1.3, m, 1H)

CH₃ (1.9, S, 3H)

H
(5.5, S, 1H)

⑫ Mol formula — $C_9H_{10}O_2$

Mass — m/z - 108 (100), 91 (80), 43 (81)

IR — 1745 cm⁻¹

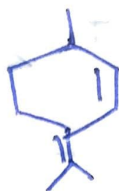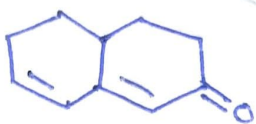NMR — δ (1.96, S, 3H), 5.00 (S, 2H), 7.22 (S, 5H)

O—CH₂—C(=O)—CH₃
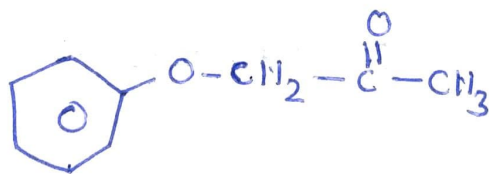
⑬ An organic compound $C_{10}H_{18}O$ upon red ⁿ followed by dehydrogenation gave 3.5-dimethylphenol ~~3,3, 55 tetramethyl cyclohexanol~~ 3-5-dimethyl phenol. The original compound had a strong band at 1720 cm⁻¹. Its NMR Spectrum had the following signals.
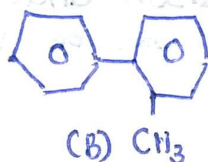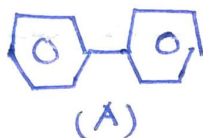
δ 1.02 (S, 12H), 1.53, S (2H), 2.06, S, 4H
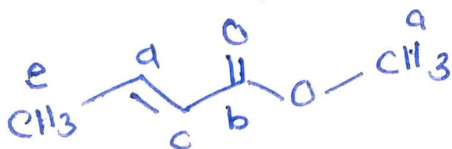
C-1255, March / April - 1992

① Calculate λ_{max}

② Explain why (B) has a UV absorption max at lower wavelength than A.

(A)   (B) CH_3

① The correct ^{13}C NMR chemical shift values of carbons labeled a-e in the following ester are

CUCIC-June-2014

a -19, b-143, C-167, d-125, e-52

a- 52, b-143, C-167, d-125, e-19

a- 52, b-167, C-143, d-125, e-19.

a- 52, b-167, C-125, d-143, e-19. ✓