

Detailed of Course Structure

Name of the Department: **Chemistry**

Name of the Programme (U.G./P.G./Ph.D.): **Post Graduate (M. Sc II and M. Sc. IV);
Under Graduate: B Sc VI Semester students may also go through it)**

Semester: **M Sc. II-Semester/M. Sc. IV (molecular Spectroscopy-one unit)**

Name of the paper/course (unit or title if there are multiple files of the same paper): **Principle of Organic Synthesis and Organic Spectroscopy/Molecular Spectroscopy/Organic Spectroscopy**

Name of the teacher: **Dr. Biswajit Maji**

Topic enclosed herewith on “Structure Determination of Organic Compounds using Spectroscopic Techniques (UV-Visible/IR/¹H-NMR/¹³C-NMR, Mass Spectrometry)

Disclaimer: There is no claim of the originality of the material and it is given only for the students to study

References:

I. Clayden Organic Chemistry

M. Sc II-Semester
Organic Spectroscopy
Unit V: Structure Determination
(Course Teacher: Dr B Maji)

1. Steps to deduce the structure of any unknown organic compound having known molecular formula and other supportive spectroscopic data and other clues:

Step 1: To determine the unknown molecular structure of any unknown compound with empirical molecular formula ($C_xH_yO_z$), first step is the identification of Double Bond Equivalent (DBEs)

Step 2: Draw all the possible structures including different isomers, different compounds those exactly match with the numbers of C, H, O and other atoms present in a formula. At the same time count the Double Bond Equivalent also.

Step 3: Try to correlate all the spectroscopic data (UV-Vis, IR, 1H -NMR, ^{13}C -NMR, 2D NMR etc, including Mass Spectrometry data etc) with all the possible structures. Finally, the best fit data to the structure will be the correct one.

Step 4: For complex molecule, the depth knowledge of spectroscopic techniques and ability to analysis of spectral data is highly fundamental in order to resolve the structural issues such as stereochemical relationship (*cis-trans* or *syn-anti* related problem), positional isomers, atom-connectivity etc.

Mostly, the presence of functional groups (alcohol or carbonyl or any other FGs) could be detected by IR spectra. Moreover, a depth knowledge of chemical shift (δ in ppm) value, multiplicity (spin-spin multiplicity), coupling constants (J values) in 1H -NMR, ^{13}C -NMR, ^{19}F -NMR, ^{31}P -NMR is very much significant. Finally, various 2D NMR (COSY, HMBC, HMQC, NOESY, ROESY etc) spectroscopy helps a lot to determine a very complicated structure.

Step I: DBEs calculation

Let us consider an organic molecule having molecular formula $C_7H_{12}O$

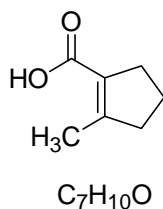
- i) Maximum number of H atoms for 7Cs $2n + 2 = 16$
- ii) Subtract the actual number of H atoms (12) i.e. $16 - 12 = 4$
- iii) Divide by 2 to give the DBEs $4/2 = 2$

Equation: $DBEs = 1/2 [2n_4 - n_1 + 2]$, where n_4 is the number of tetravalent atoms (C), n_1 is the number of hydrogen

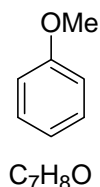
Now apply for $C_7H_{12}O$,

$$DBEs = 1/2 [7 \times 2 - 12 + 2] = 1/2 [16 - 12] = 1/2 [4] = 2$$

Other examples:



DBEs = 3
One for carbonyl (C=O)
One for double bond
One for ring
Total = 3

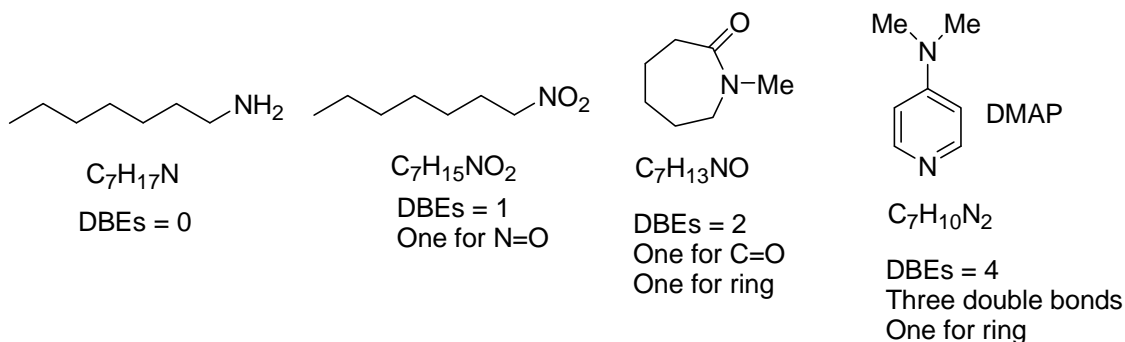


DBEs = 4
Three double bonds
One ring structure
Total = 4

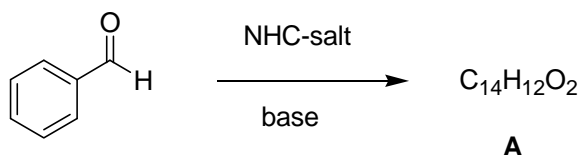
If, N is present in unknown organic compound, the double bond equivalent identification is not following the same as above. DBEs identification for nitrogen containing compounds follows as below:

Equation: $DBEs = 1/2 [2n_4 - n_1 + n_3 + 2]$, where n_4 is the number of tetravalent atoms (C), n_1 is the number of hydrogen (H), n_3 is the number of trivalent atoms (N).

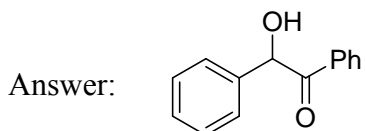
Applying the equation for the following nitrogen containing organic compounds and let see the identification of DBEs;



2. A compound having molecular formula $C_{14}H_{12}O_2$ obtained by a following reaction and shows the following proton NMR. Suggest a structure of an organic compound A.



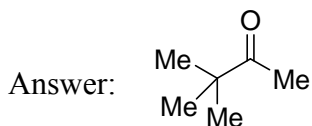
1H NMR: δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.46-7.20 (m, 7H), 5.96 (s, 1H), 4.59 (bs, 1H). Disappear the peak at 4.59 on addition of D_2O .



3. An organic compound A having molecular formula $C_6H_{12}O$ shows the following proton NMR. Suggest a structure of an organic compound A.

IR (cm^{-1}): 1715

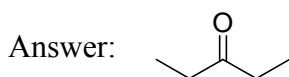
1H NMR: δ 2.1 (s) and 1.2 (s)



4. $C_5H_{10}O$

IR (cm^{-1}): 1715

1H NMR: (3H, Triplet), (2H, Quartet)

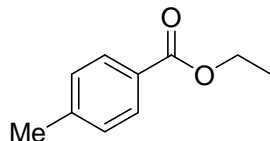


5. C₁₀H₁₂O₂

IR (cm⁻¹): 3076, 2920, 1717, 1040

¹H NMR: δ 7.90 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.28 (q, 2H), 2.40 (s, 3H), 1.45 (t, 3H)

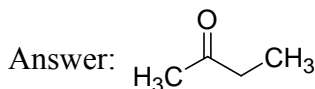
Answer:



6. C₅H₁₀O

IR (cm⁻¹): 1715

¹H NMR: δ 2.40 (t, 2H), 2.12 (s, 3H), 1.2 (m, 2H), 0.95 (t, 3H)

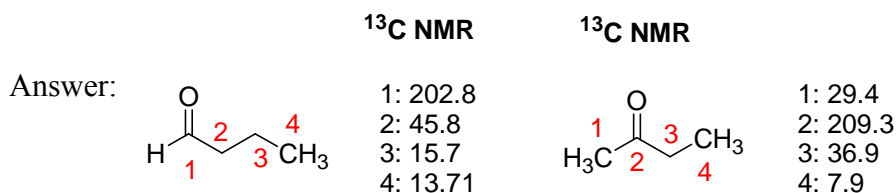


5. A compound of molecular formula C₄H₈O gave the following ¹³C and IR data.

IR: 1730 cm⁻¹

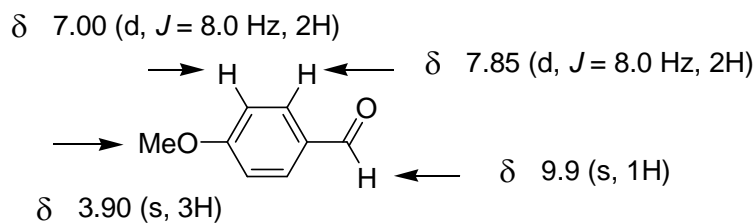
¹³C: δ 201.6, 45.8, 15.7 and 13.7.

Deduce the structure.



7. An organic compound (molecular formula C₈H₈O₂) shows a strong signals in IR spectrum at 1684cm⁻¹ while in ¹H NMR spectrum the protons appeared as follows: ¹H NMR (CDCl₃, 400 MHz): δ 9.9 (1H, s), 7.85 (2H, d), 7.00 (2H, d), 3.90 (s, 3H). Deduce the structure.

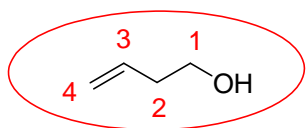
Answer: DBE = 5



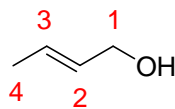
8. Three compounds of molecular formula C_4H_8O gave the following ^{13}C and IR data.
- Compound **A**: IR (3200 broad cm^{-1})
: ^{13}C NMR (δ 134.7, 117.2, 61.3 and 36.9)
- Compound **B**: IR (No peaks except CH and fingerprint)
: ^{13}C NMR (δ 67.9 and 25.8)
- Compound **A** reacts with hydrogen over a palladium catalyst to give the product **C** of molecular formula $C_4H_{10}O$, IR 3200 (broad) cm^{-1} and ^{13}C NMR δ 62.9, 36.0, 20.3 and 15.2.
- Deduce the structures for Compound **A**, **B** & **C**.

Answer: P. T. O.

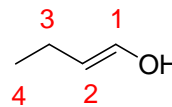
Structure A Could be:



^{13}C NMR



^{13}C NMR



^{13}C NMR

Expected δ value in ppm:

1: 61.3
2: 36.9
3: 134.7
4: 117.2

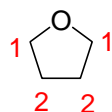
Compound A

1: 62.9
2: 132.7
3: 128.5
4: 18.3

The above structure is enol and enol carbon (1) appear in the range of 160-170. So, It could not be the compound

Match with given ^{13}C -data
So the compound would be
but-3-ene-1-ol

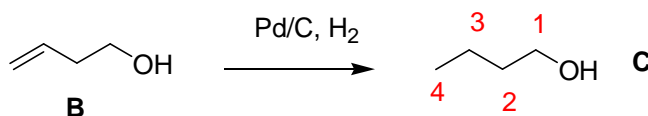
Compound B: No characteristic IR data, except CH-stretching frequency and fingerprint region. In ^{13}C -NMR, only two peaks, 67.9 and 25.8, Therefore, the compound could be THF i.e Tetrahydrofuran.



^{13}C NMR δ value:

1: 67.9
2: 25.8

Compound C:

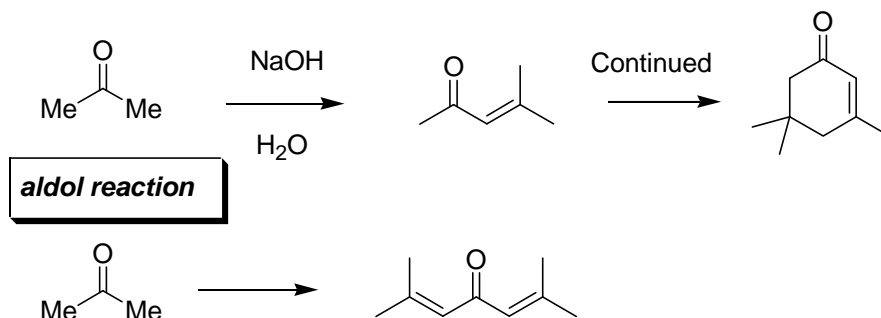


^{13}C NMR δ value:

1: 62.9
2: 36.0
3: 20.3
4: 15.2

9. When acetone is treated with base, a higher boiling liquid is obtained from the reaction mixture. The spectroscopic data of the liquid are: infrared, 1620 cm^{-1} , 1695 cm^{-1} ; $^1\text{H-NMR}$ spectra: δ 1.9 (3H, s), 2.1 (6H, s), 6.15 (1H, s); Mass: m/z (RA), 55 (100), 83 (90); $^{13}\text{C NMR}$: δ 20, 27, 31, 124, 154 and 197. Deduce the structure.

Answer:

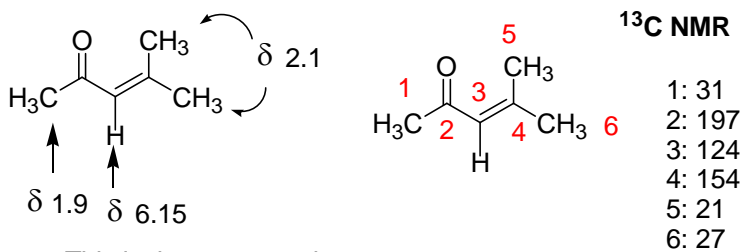


Proposed Spectroscopic data:

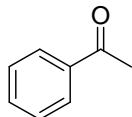
IR : 1620 and 1695 cm^{-1}

$^1\text{H-NMR}$: δ in ppm: 6.15 (s, 1H), 2.1 (s, 6H), 1.9 (s, 3H)

$^{13}\text{C NMR}$: δ 197, 154, 124, 31, 27, 21



10.



Excess NaOH

$\text{C}_{24}\text{H}_{18}$

MS: M^+ 306

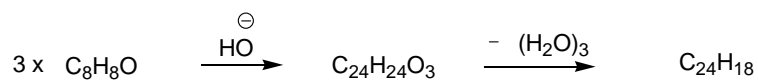
IR: 1600 and 1500 cm^{-1}

$^1\text{H NMR}$: δ 8.05 (3H, s), 7.64 (6H, d, $J = 6\text{ Hz}$ and 7.5-7.3 (9H, m)

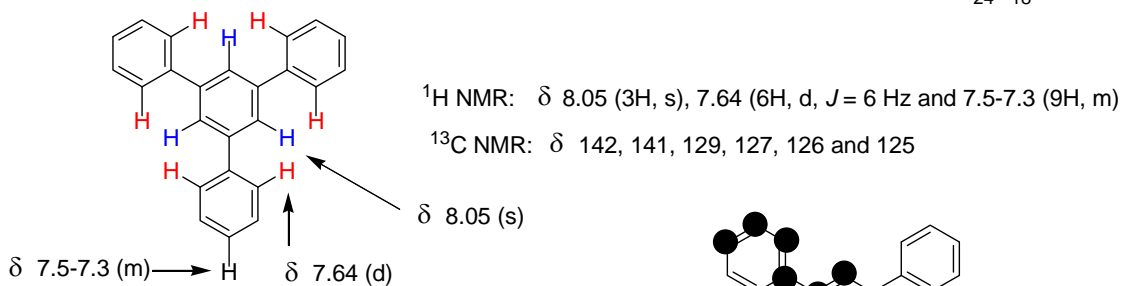
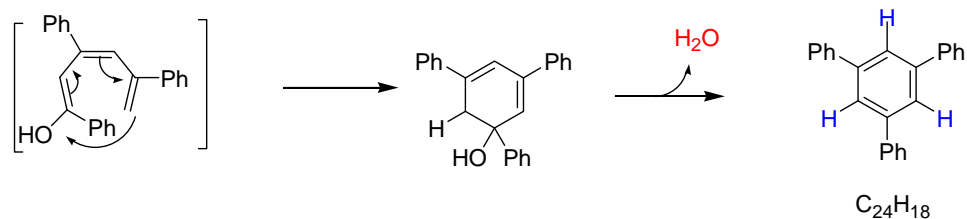
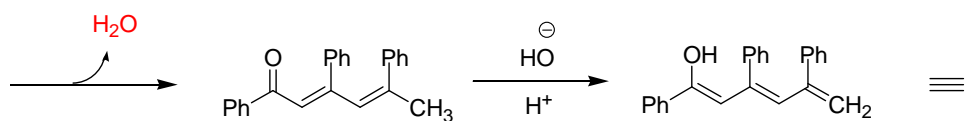
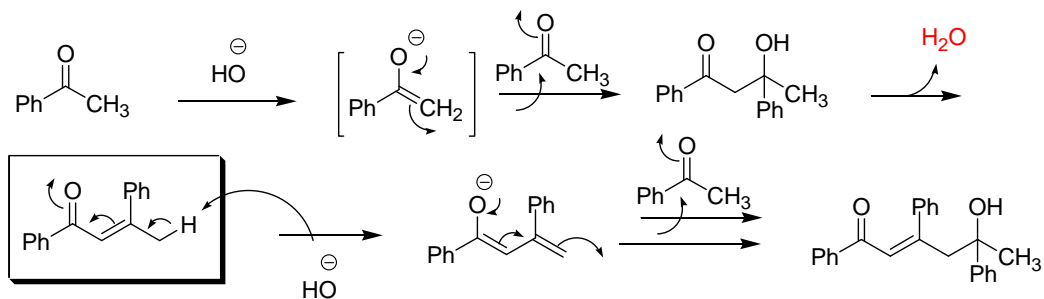
$^{13}\text{C NMR}$: δ 142, 141, 129, 127, 126 and 125

Deduce the structure for the following said reaction matching all spectroscopic data.

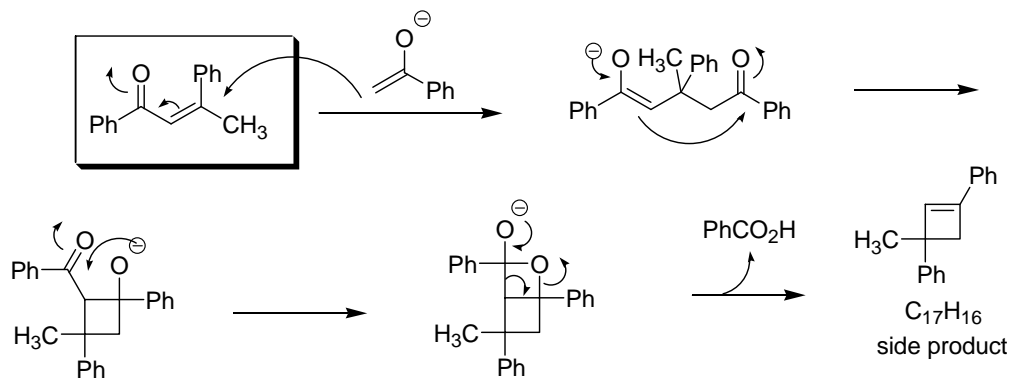
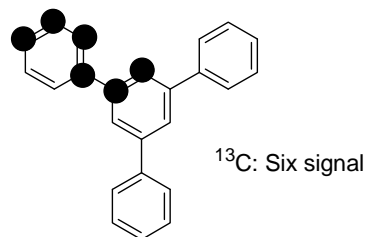
Answer: DBE = 16



Possible compounds obtained through base-catalyzed / or acid-catalyzed condensation reaction:



^1H : Four non-equivalent protons



11. An organic compound (molecular formula $C_8H_8O_2$) shows a strong signals in IR spectrum at 1684cm^{-1} while in ^1H NMR spectrum the protons appeared as follows: ^1H NMR (CDCl_3 , 400 MHz): δ 9.9 (1H, s), 7.85 (2H, d), 7.00 (2H, d), 3.90 (s, 3H). Deduce the structure.

Answer: See before problem No: 6

12. An organic compound having molecular formula C_5H_8O gives positive iodoform test. It shows the following spectral data:

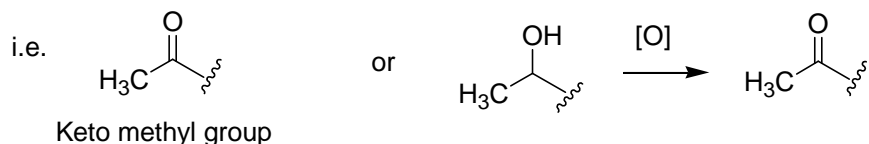
UV: λ_{max} 277 nm ϵ_{max} 4600

IR: Among other peaks a more prominent band at 1685 cm^{-1}

NMR: Four nonequivalent proton signals. Deduce the structure of the compound.

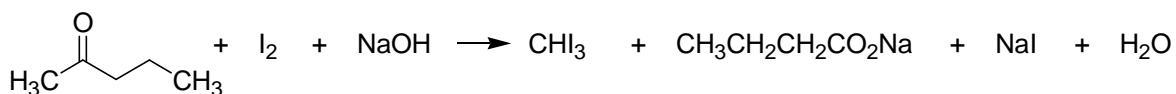
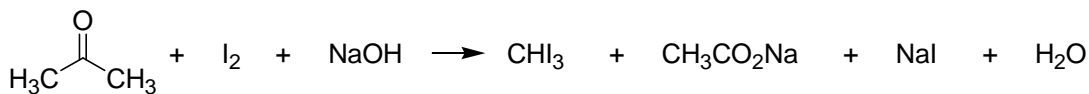
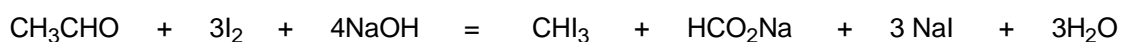
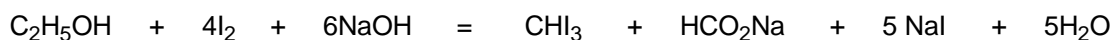
Answer:

Iodoform reaction is given by a compound having either $\text{CH}_3\text{-CO-}$ group or $\text{CH}_3\text{-CH(OH)-}$ group



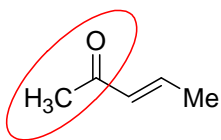
1° alcohol \longrightarrow Only ethanol

ethanal, acetone, 2-pentanone etc give the iodoform test as shown below:

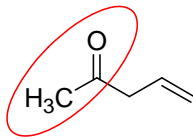


C_5H_8O ; DBE = 2

i.e. The probable compound could be:



or



Estimated:

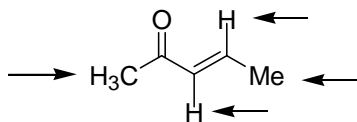
UV: 270-280 nm

IR: $\sim 1680\text{ cm}^{-1}$

Estimated:

UV: 230-243 nm

IR: 1710 cm^{-1}



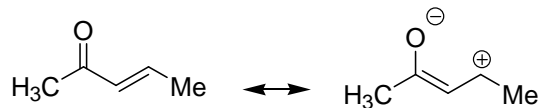
Four non-equivalent protons are there.

As suggested the spectroscopic data,

UV-Vis : 277 nm

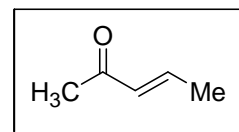
IR: 1685 cm^{-1}

$^1\text{H-NMR}$: Four non-equivalent protons



Thus, carbonyl stretching frequency is reduced

Therefore the compound is :

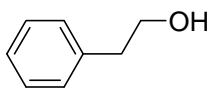


13. $C_8H_{10}O$: 4 degrees of unsaturation. • Infrared Spectrum: 3500, 3028, 1800-1950 cm^{-1} . • $^1\text{H NMR}$ Spectrum: δ 7.35-7.15 (m, 5H), two 2H-protons triplets, ~ 2.0 (broad singlet, 1H), $^{13}\text{C NMR}$ Spectrum: 138.7, 129.1, 128.5, 126.4, 63.5, and 39.2. Deduce the structure.

Answer:

$C_8H_{10}O$; DBE = 4

i.e. The probable compound could be:

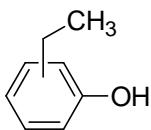


Estimated:

IR: 3500, 3028 cm^{-1}

$^1\text{H-NMR}$ (in ppm):

δ 7.40-7.10 (m, 5H), 3.78 (t, 3H), 2.80 (t, 3H), ~ 2.0 -3.0 (bs, 1H)

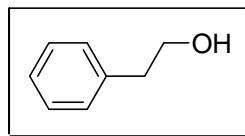


o, *m* or *p*

Estimated:

If, substituted phenol then, four aromatic proton must be there. two methylene proton resonates as quartet and methyl protons appear as triplet.

Therefore the compound is :



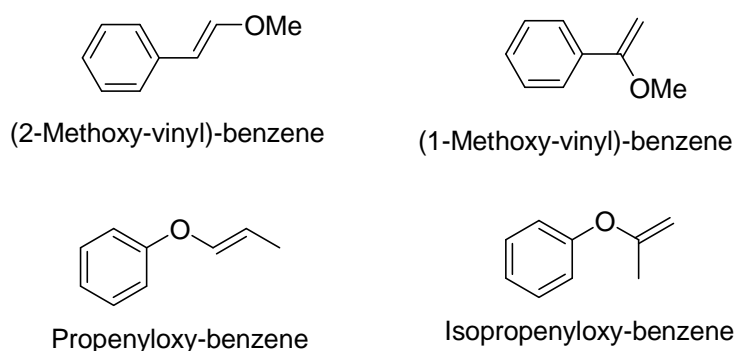
14. A compound $C_9H_{10}O$ reacts with aq. $KMnO_4$. The compound shows the following 1H NMR spectroscopic data:

1H NMR: two doublets at δ 5.2 and 6.1 and each doublet appeared in J value 17.6 Hz; five aromatic protons at the range δ 7.12-7.58 ppm; three protons appeared at δ 3.7 ppm.

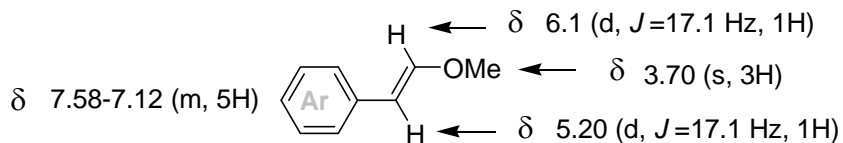
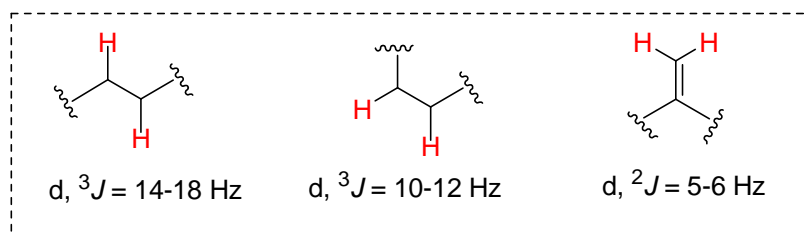
IR: No characteristic peaks at 3400 cm^{-1} and 1700 cm^{-1} .

Answer:

$C_9H_{10}O$; DBE = 5, as IR data suggests that no presence of carbonyl and free OH group present in the compound structure; thus, the possible compound structure might be as follows:

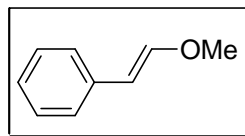


1H NMR (in ppm): 2 doublets at 5.2 and 6.1; $J = 17.6\text{ Hz}$ i.e indicates *trans*-olefin
5 ArH at 7.12-7.58
3 H at 3.70

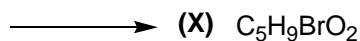
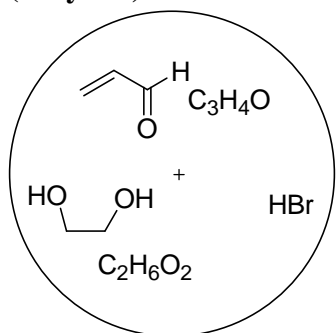


No characteristics carbonyl and OH-stretching frequency

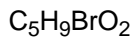
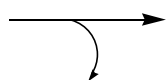
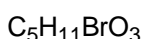
Therefore the compound is :



15. Follow the below reaction scheme and other clues and determine the structure of **X** (Clayden)

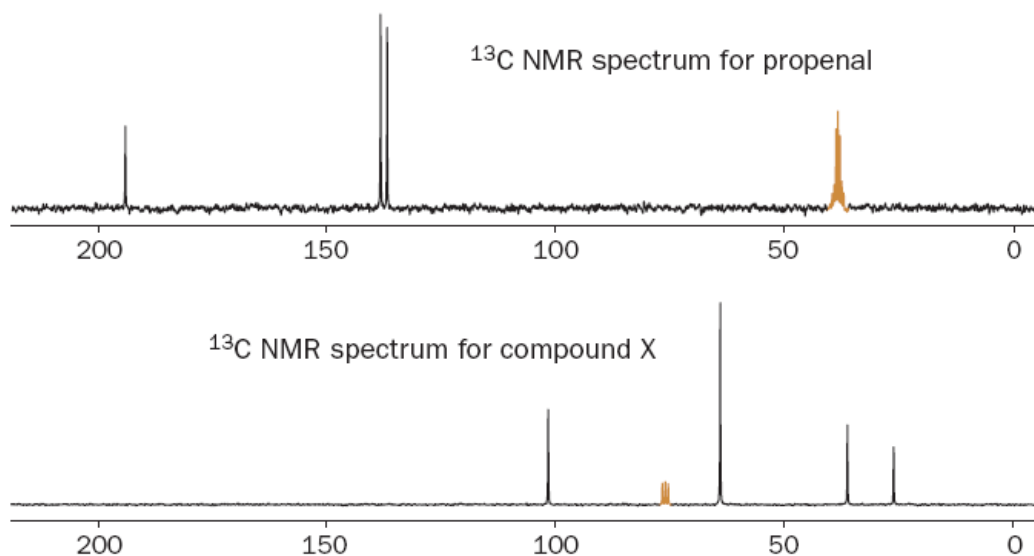


IR: No OH, no carbonyl, no alkene related stretching frequency were observed; 1128 cm^{-1}



^{13}C NMR: See the spectrum as below
 $m/z = 181, 73$ (100%)

Deduce the structure of **X**.



Answer: The ^{13}C -NMR spectrum of $\text{CH}_2=\text{CH}-\text{CHO}$ i.e. propenal clearly shows one carbonyl group and two carbons on a double bond. These have all disappeared in the product and for the five carbon atoms we are left with four signals, two saturated, one next to oxygen, and one at 102.6 ppm. just creeping into the double bond region. It can't be an alkene as an alkene is impossible with only one carbon atom! The IR spectrum gives us another puzzle—there appear to be no functional groups at all! No OH, no carbonyl, no alkene—what else can we have?

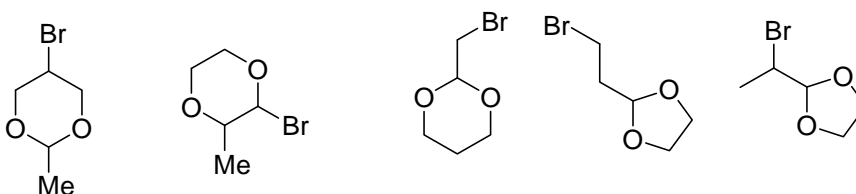
Anyway, the DBEs identified from molecular formula of the product (X) is 1 (One).

Compound having halogen (F, Cl, Br) the DBE or IHD (Index Hydrogen Deficiency) can be calculated as follows, For $C_5H_9BrO_2$

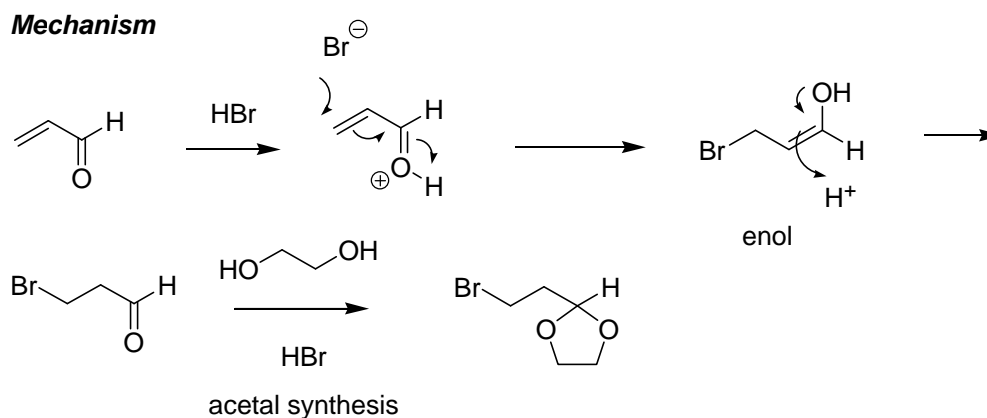
IHD or DBE = $1/2 [2n_C - n_H - n_X + 2]$; n_H = number of hydrogen, n_X = number of halogen.

$$\text{IHD/DBE} = 1/2 [2 \times 5 - 9 - 1 + 2] = 1/2 [12 - 10] = 2/2 = 1$$

The index Hydrogen Deficiency value clearly indicates that in the structure X has one ring structure. The possible structures with the molecular formula $C_5H_9BrO_2$ may represent as follows: (NB: IR and ^{13}C data indicates there is no chances of double bond in the X).

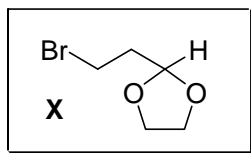


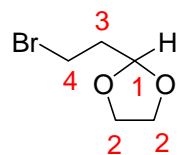
Applying basic knowledge of organic chemistry, one may propose a mechanism for the reaction scheme which is shown below,



A decision can easily be reached from the base peak in the mass spectrum at 73. This is a fragment corresponding to the five-membered ring and not to the six-membered ring.

Therefore the X is:





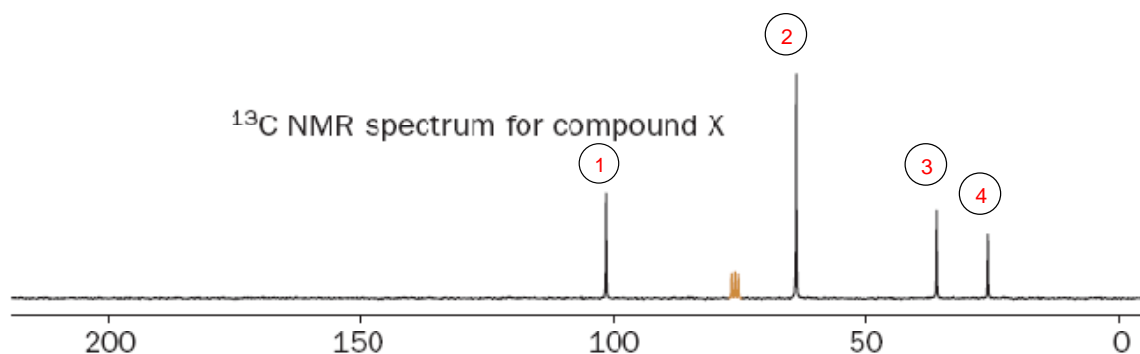
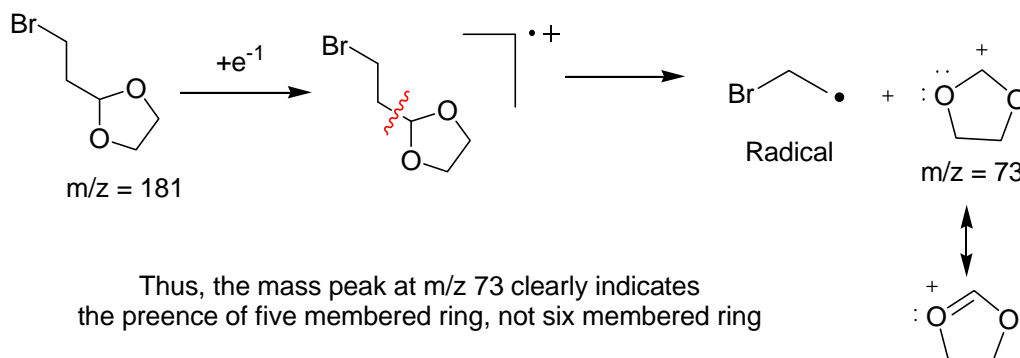
$m/z = 181, 73$ (100%)

IR (cm^{-1}): 1128 which represent C-O stretching frequency

^{13}C NMR (ppm): As assigned in below spectrum

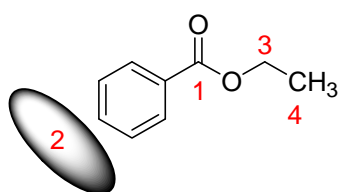
$\text{C}_5\text{H}_9\text{BrO}_2$
Mol. Wt.: 181.0278

Mass spectra analysis is finally reached at decision (see the fragmentation)



16. The ^{13}C NMR spectrum for ethyl benzoate contains these peaks: 17.3, 61.1, 100–150 p.p.m. (four peaks), and 166.8 p.p.m. Which peak belongs to which carbon atom?

Answer:



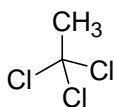
^{13}C NMR (ppm):

- 1: 166.8 (C=O)
- 2: 100-150 (Aromatic carbon)
- 3: 61.1 (O-CH₂)
- 4: 17.3 (CH₃)

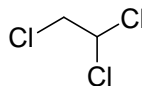
17. The thinner used in typists' correction fluids is a single compound, $C_2H_3Cl_3$, having ^{13}C NMR peaks at 45.1 and 95.0 p.p.m. What is its structure? A commercial paint thinner gives two spots on thin layer chromatography and has ^{13}C NMR peaks at 7.0, 27.5, 35.2, 45.3, 95.6, and 206.3 p.p.m. Suggest what compounds might be used to make up this thinner.

Answer:

DBE = 0, so no double bond and of course there is question about ring structure, as two carbon atoms are there. So possible structures would be as follows:



or



^{13}C NMR (ppm):

(estimated)

Methyl carbon would be in the any range of 18 – 50 ppm and CCl_3 carbon should resonate at much higher chemical shift say, 50 – 100 ppm range, as three -Cl atoms are joined.

^{13}C NMR (ppm):

(estimated)

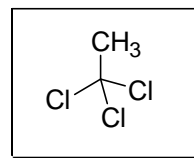
$-CH_2Cl$ carbon would be in the range of 50– 100 ppm and $-CHCl_2$ carbon should resonate at higher chemical shift, but the two shifts would not be so far apart.

^{13}C NMR (ppm):

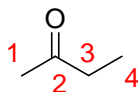
Actual δ value in ppm:

45.1 and 95.0 p.p.m

Thus, the compound $C_2H_3Cl_3$ will be:



In part II, the mixture probably contains the same trichloroethane as the similar peaks were found at δ 45.3 and 95.6 (ppm). The remaining peaks are at δ 7.0, 27.5, 35.2, and 206.3 (ppm) suggest that a ketone. In fact 2-butanone structure fit the data as below:



^{13}C NMR (ppm):

1: 27.5 ($CH_3C=O$)

2: 206.3 ($C=O$)

3: 35.2 ($COCH_2CH_3$)

4: 7.0 (CH_3)

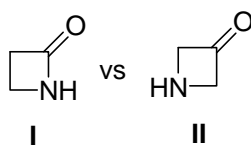
18. Four compounds, each having the formula C_3H_5NO , have the IR spectra summarized here. What are their structures? Without ^{13}C NMR data, it may be easier to tackle this problem by first writing down all the possible structures for C_3H_5NO . In what specific ways would ^{13}C NMR data help?

- A) One sharp band above 3000 cm^{-1} ; one strong band at about 1700 cm^{-1}
- B) Two sharp bands above 3000 cm^{-1} ; two bands between 1600 and 1700 cm^{-1}
- C) One strong broad band above 3000 cm^{-1} ; a band at about 2200 cm^{-1}

Answer:

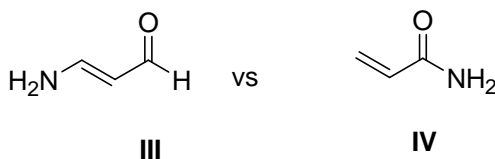
“N”-atom is here, so DBEs = 2

A. The possible structures would be as follows:



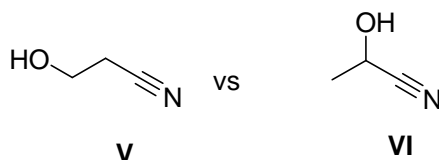
As depicted in question part A, the A) One sharp band above 3000 cm^{-1} , might be NH stretching frequency; one strong band at about 1700 cm^{-1} , which would be of course carbonyl stretching frequency. In the above two probable structures, β -lactam carbonyl should appear at higher value than 1700 cm^{-1} . Thus, the best fit the structure II, although, ^{13}C -NMR spectral data give the confirmed structure. Because, in ^{13}C NMR amide carbonyl carbon and ketone carbonyl carbon chemical shifts have two different values.

B. The possible structure would be as follows:



As depicted in question part B, Two sharp band above 3000 cm^{-1} , might be NH_2 stretching frequency (one for symmetrical stretching and another for antisymmetrical stretching). Other strong bands at 1600 to 1700 cm^{-1} , which would be of course one for carbonyl ($C=O$) and other for olefin ($C=C$) stretching frequency. Therefore, the possible structures are III or IV. ^{13}C -NMR definitely could help to solve which one is the correct one, as amide carbonyl ($C=O$) and aldehydic carbonyl carbon have different chemical shift.

- C. One strong broad band above 3000 cm^{-1} ; a band at about 2200 cm^{-1}
Thus, the probable structures would be as follows:



As depicted in question part C, one broad band at above 3000 cm^{-1} , might be -OH stretching frequency. Other strong bands at 2300 cm^{-1} , which would be, of course, for one triple bond. Therefore, the possible structures are **V** or **VI**. ^{13}C -NMR definitely could help to solve which one is the correct one, as shown in str. **VI**, the carbon attached with one -OH and one -CN (EWG) groups resonates at higher chemical shift.

19. Three compounds of molecular formula $\text{C}_4\text{H}_8\text{O}$ have the IR and ^{13}C NMR spectra given below. Suggest a structure for each compound, explaining how you make your deductions.

Compound **A**: IR: 1730 cm^{-1} ; ^{13}C NMR: 13.3, 15.7, 45.7, and 201.6 p.p.m.

Compound **B**: IR: 3200 (broad) cm^{-1} ; ^{13}C NMR: 36.9, 61.3, 117.2, and 134.7 p.p.m.

Compound **C**: IR: no peaks except CH and fingerprint; ^{13}C NMR: 25.8 and 67.9 p.p.m.

Compound **D**: IR: 3200 (broad) cm^{-1} ; ^{13}C NMR: 15.2, 20.3, 36.0, and 62.9 p.p.m.

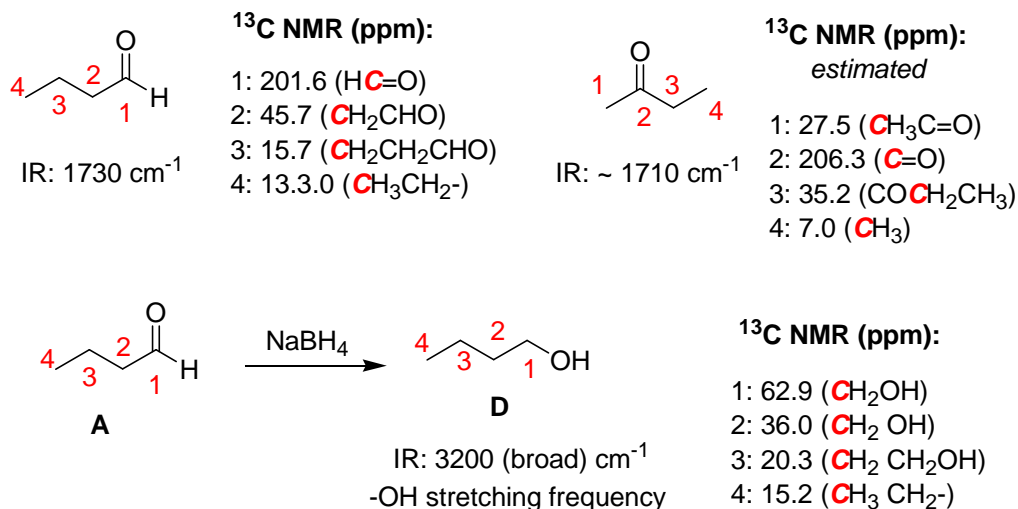
Compound **A** reacts with NaBH_4 to give compound **D**. Compound **B** reacts with hydrogen gas over a palladium catalyst to give the same compound **D**. Compound **C** reacts with neither reagent. Suggest a structure for compound **D** from the data given and explain the reactions. (Note. H_2 reduces alkenes to alkanes in the presence of a palladium catalyst.)

Answer:

The DBE for the molecular formula $\text{C}_4\text{H}_8\text{O}$ is 1 (ONE).

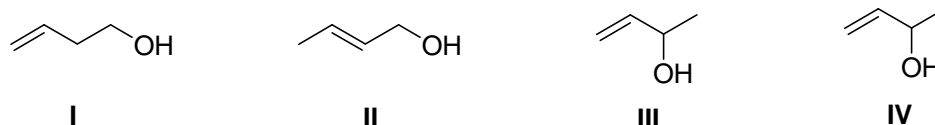
Compound **A**:

IR: 1730 cm^{-1} , that implies that the compound **A** contain carbonyl group and another clue is the reduction by NaBH_4 suggests the presence of aldehyde functionality which further again confirmed by ^{13}C -NMR at δ 201.6 ppm. Thus, the compound could be butanal.

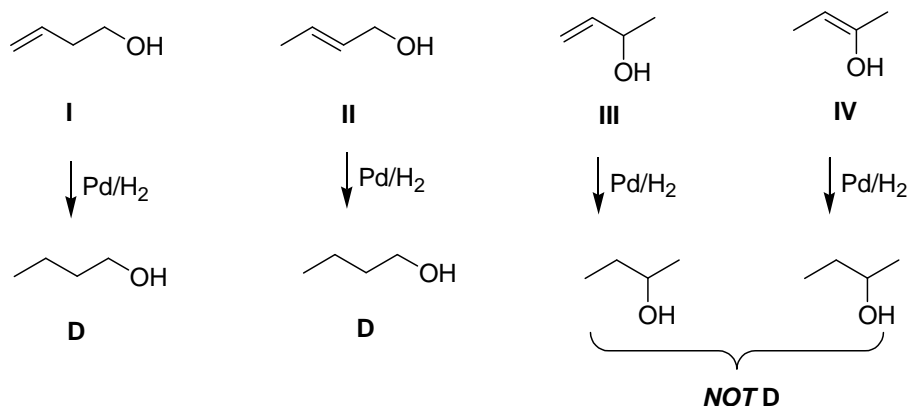


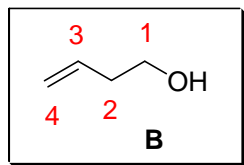
Compound **B**: IR: 3200 (broad) cm⁻¹; ¹³C NMR: 36.9, 61.3, 117.2, and 134.7 p.p.m.

Compound **B** appears a broad peak at 3200 (broad) cm⁻¹ in IR spectrum, suggest a free -OH functional group. In ¹³C NMR, it is clear one unsaturation double bond i.e. olefin is present in compound **B** and the olefin carbons resonate at δ 134.7 and 117.2 ppm. The probable structures would be as follows:



Among the above structures, compound **III** and **IV** would not be as on treatment with Pd/H₂ affords secondary alcohol which is not the same as the compound **D**. Between the compound **I** and **II**, compound **I** would be as the olefin carbons resonate at unequal δ 134.7 and 117.2 ppm value. In compound **II**, equal substitution pattern might be resulted the alkene carbons resonate at a very close δ values.



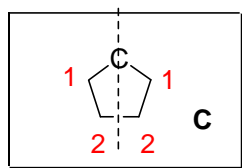


IR: 3200 (broad) cm^{-1} ;

^{13}C NMR (ppm):

- 1: 61.3 (CH_2OH)
- 2: 36.9 ($\text{CH}_2\text{CH}_2\text{OH}$)
- 3: 134.7 ($\text{CH}_2=\text{CH}-$)
- 4: 117.2 ($\text{CH}_2=\text{CH}-$)

Compound **C**: IR: no peaks except CH and fingerprint; ^{13}C NMR: 25.8 and 67.9 p.p.m. In IR spectrum, there are no characteristic functional groups peaks were observed. In ^{13}C NMR spectrum, only two peaks at δ 25.8 and 67.9 suggest the compound **C** would be symmetric. One important another clue is that it has one DBE without any unsaturation which only possible to think THF i.e. tetrahydrofuran.



IR: **NO** FG peaks

^{13}C NMR (ppm):

- 1: 67.9 (OCH_2)
- 2: 28.9 ($-\text{CH}_2\text{CH}_2-$)

20. You have dissolved *t*-BuOH (Me_3COH) in MeCN with an acid catalyst, left the solution overnight, and found crystals with the following characteristics there in the morning. What are they?

IR: 3435 and 1686 cm^{-1}

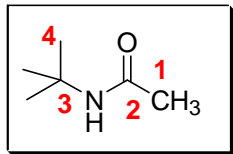
^{13}C NMR: 169, 50, 29, and 25 p.p.m.

Mass spectrum (%): 115 (7), 100 (10), 64 (5), 60 (21), 59 (17), 58 (100), and 56 (7). (Don't try to assign all of these!)

Answer:

The peaks at 3435 and 1686 cm^{-1} in IR spectrum suggest that the compound having characteristic amide NH ($-\text{CONHR}$) and carbonyl ($-\text{CONHR}$) stretching frequency. If you dissolved *t*-BuOH (Me_3COH) in MeCN with an acid catalyst, left the solution overnight, the following compound would be formed.

Mechanism:



IR: 3435 (NH-stretching frequency and 1686 (amide carbonyl stretching frequency in cm^{-1})
Mass: M^+ (115), 100 (10), 58 (100)

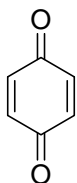
^{13}C NMR (ppm):

- 1: 29 (-CO C_1H_3)
- 2: 169 (-NH C_2OCH_3)
- 3: 50 [$(\text{CH}_3)_3\text{C}$ -]
- 4: 25 [$(\text{CH}_3)_3\text{C}$ -]

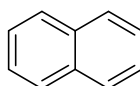
21. How many signals would you expect in the ^{13}C NMR of the following compounds?



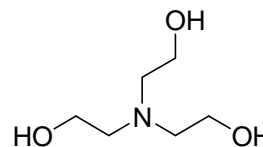
Adamantane



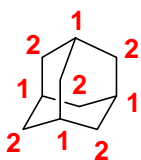
p-Benzoquinone



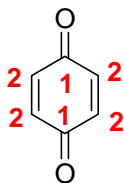
Naphthalene



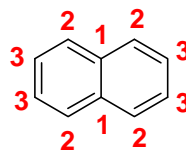
Answer:



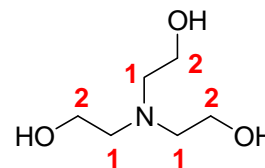
Adamantane
Two signals (^{13}C)



p-Benzoquinone
Two signals (^{13}C)

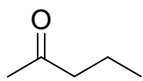


Naphthalene
Threesignals (^{13}C)

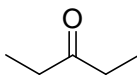


Two signals (^{13}C)

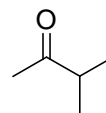
22. How would mass spectra help you distinguish these structures?



$\text{C}_5\text{H}_{10}\text{O}$
Mol. Wt.: 86.1323



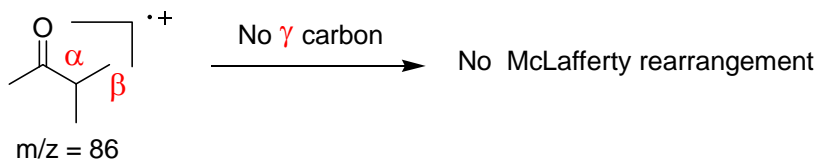
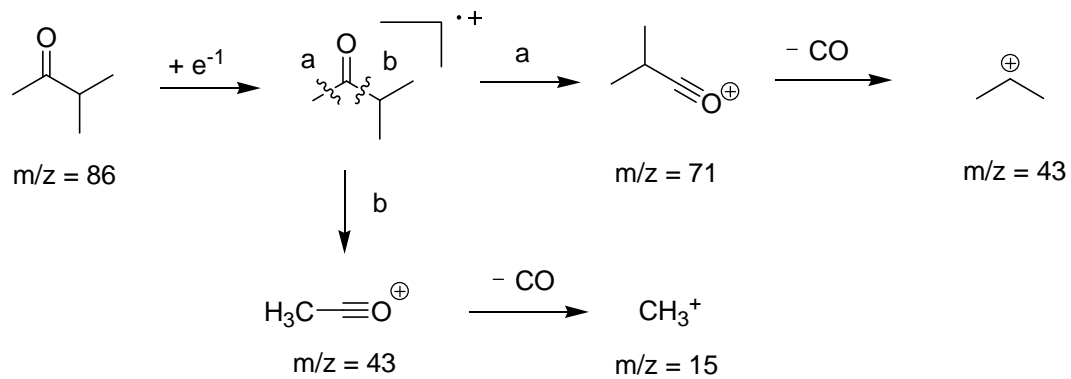
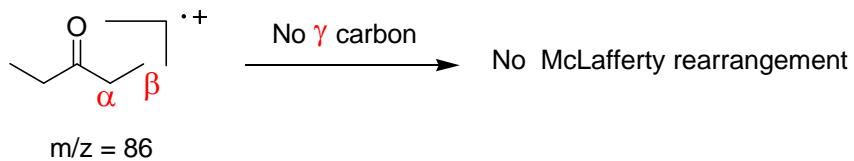
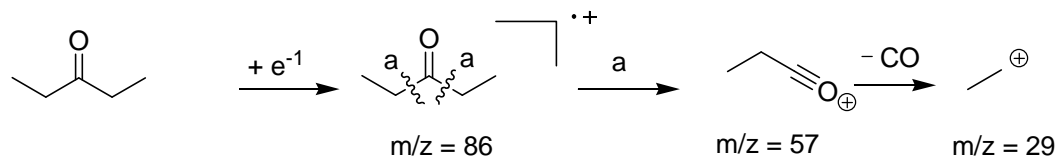
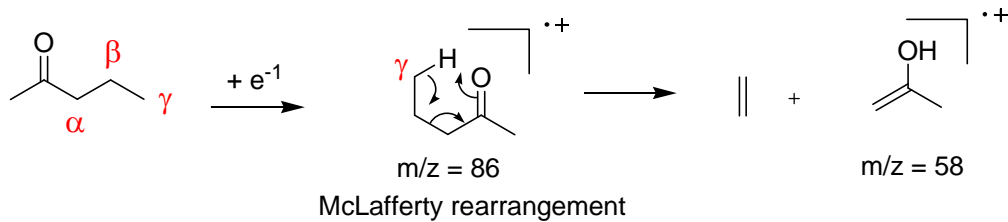
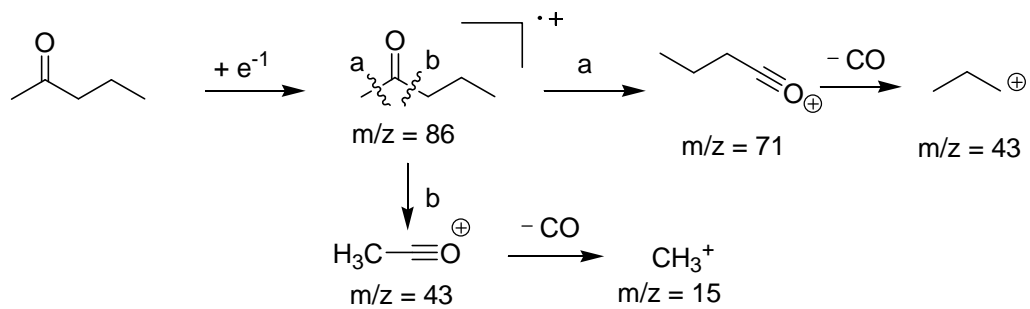
$\text{C}_5\text{H}_{10}\text{O}$
Mol. Wt.: 86.1323



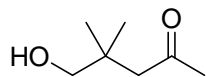
$\text{C}_5\text{H}_{10}\text{O}$
Mol. Wt.: 86.1323

Answer:

Above three ketones are isomers of same molecular formula $\text{C}_5\text{H}_{10}\text{O}$. These three isomers can be easily distinguished by the Mass spectra. The fragmented mass peaks for each ketone appeared at m/z value which is follows:



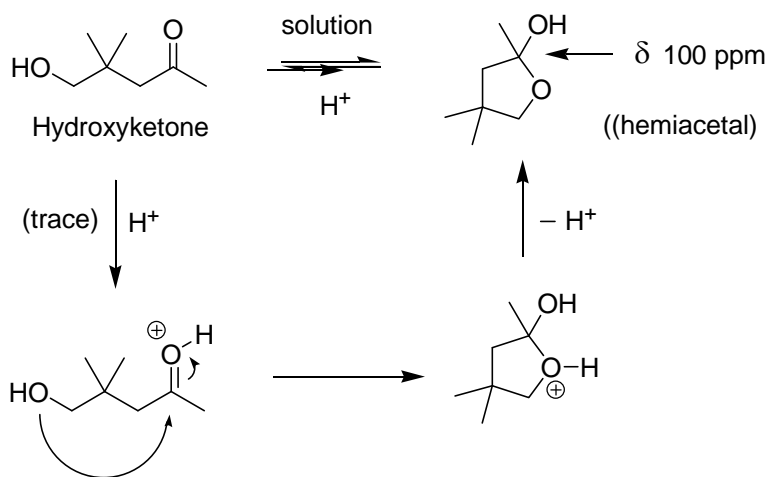
23. The following hydroxyketone shows no peaks in its infrared spectrum between 1600 and 1800 cm^{-1} but it does show a broad absorption at 3000 to 3400 cm^{-1} . In the ^{13}C NMR spectrum, there are no peaks above 150 p.p.m. but there is a peak at 110 p.p.m. Suggest an explanation.



Hydroxyketone

Answer:

In the hydroxyketone structure, there are one ketone ($\text{C}=\text{O}$) functional group and one $-\text{OH}$ functional group. In a solution, in fact, the hydroxyketone exists in a cyclic hemiacetal form (see below scheme) and as a result, no characteristic ketone carbonyl stretching frequency at the range of $\sim 1700 \text{ cm}^{-1}$ was observed. The equilibrium favors towards right side and which is again ascertained by spectral analysis (^{13}C -NMR). In the ^{13}C NMR spectrum, there are no peaks above 150 p.p.m. but there is a peak at 110 p.p.m. No peaks at above δ 150 p.p.m. indicate no carbonyl functional group exists in a solution of hydroxyketone substrate. A peak at 110 p.p.m. suggests an alkene or a carbon bonded with two oxygen (hemiacetal/acetal type compound). Dehydration step for this substrate is not a easy task, in fact, in the presence of trace acid (H^+), the substrate hydroxyketone rather easily from hemiacetal (Scheme below). The hemiacetal fits all the spectroscopic data in a correct manner.

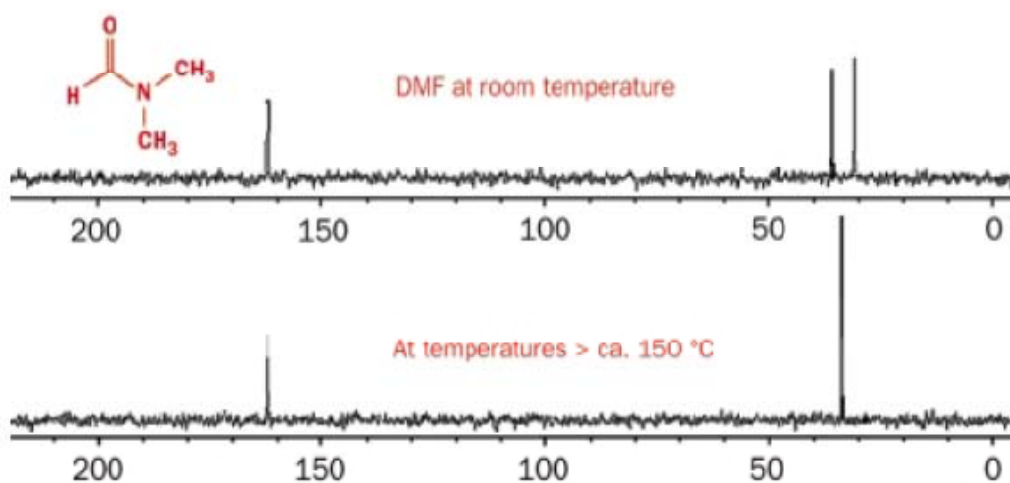


24. At room temperature, DMF shows three signals and at higher temperature the DMF shows only two signals in ^{13}C -NMR. Explain the fact.

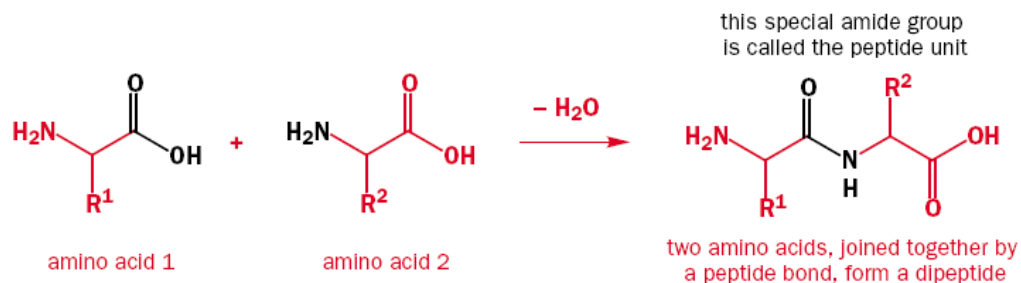
Answer: (From clayden)

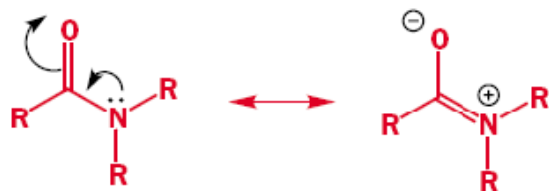
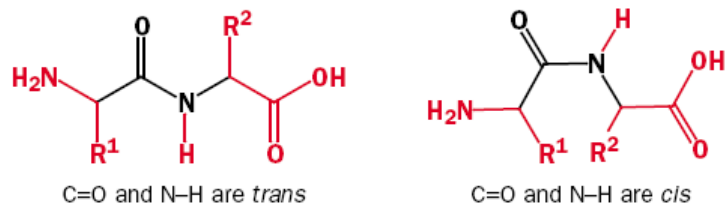
The $\text{C}-\text{N}$ bond length to the carbonyl group is closer to that of a standard $\text{C}-\text{N}$ double bond (127 pm) than to that of a single bond (149 pm). This partial double bond

character is responsible for the restricted rotation about this C–N bond. We must supply 88 kJ mol⁻¹ if we want to rotate the C–N bond in DMF (remember a full C–C double bond takes about 260 kJ mol⁻¹). This amount of energy is not available at room temperature and so, for all intents and purposes, the amide C–N bond is locked at room temperature as if it were a double bond. This is shown in the carbon NMR spectrum of DMF. How many carbon signals would you expect to see? There are three carbon atoms altogether and three signals appear—the two methyl groups on the nitrogen are different. If free rotation were possible about the C–N bond, we would expect to see only two signals. In fact, if we record the spectrum at higher temperatures, we do indeed only see two signals since now there is sufficient energy available to overcome the rotational barrier and allow the two methyl groups to interchange



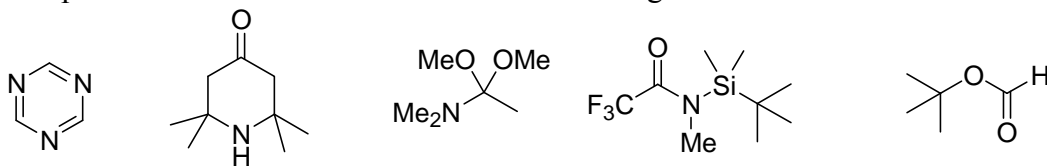
Look at protein structure????



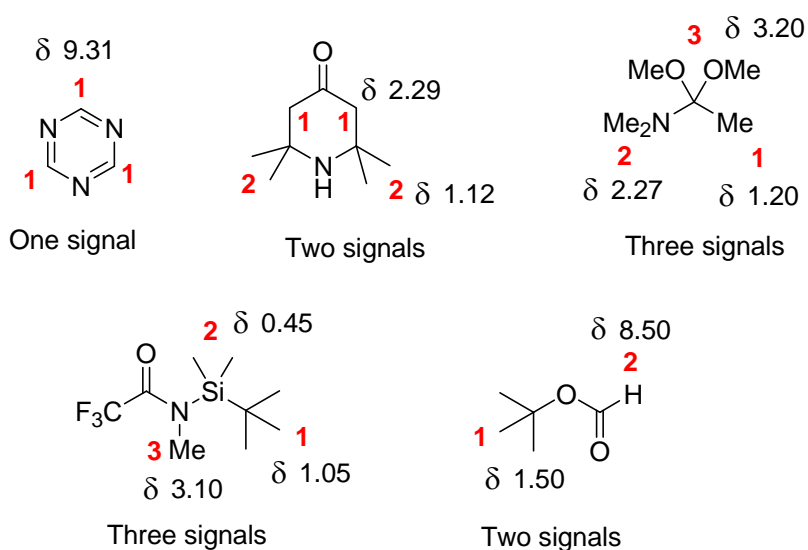


the oxygen atom's withdrawal of electrons
weakens the carbonyl bond

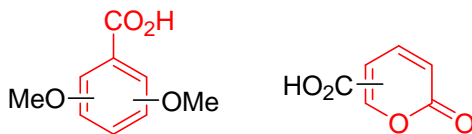
25. How many signals will there be in the ^1H NMR spectrum of each of these compounds? Estimate the chemical shifts of the signals.



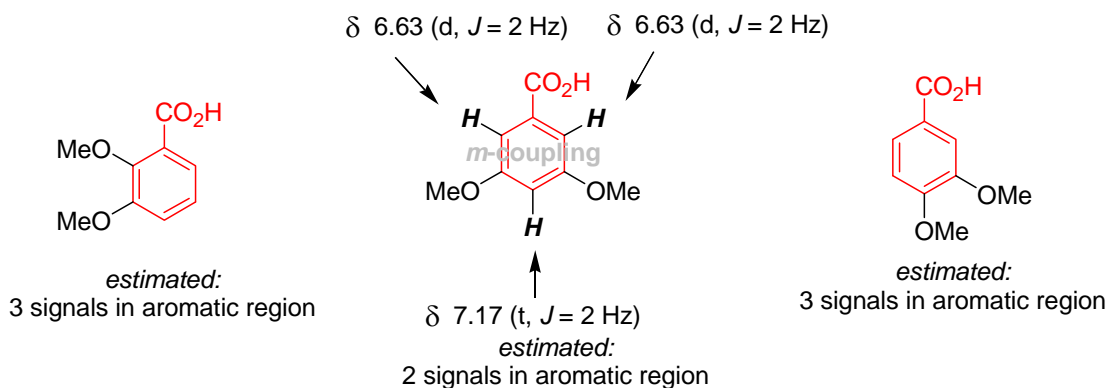
Answer:



26. One isomer of dimethoxybenzoic acid has the ^1H NMR spectrum 3.85 (6H, s), 6.63 (1H, t, $J = 2$ Hz), 7.17 (2H, d, $J = 2$ Hz) and one isomer of coumalic acid has the ^1H NMR spectrum 6.41 (1H, d, $J = 10$ Hz), 7.82 (1H, dd, $J = 2, 10$ Hz), 8.51 (1H, d, $J = 2$ Hz). In each case, which isomer is it? The substituents in black can be on any carbon atoms.

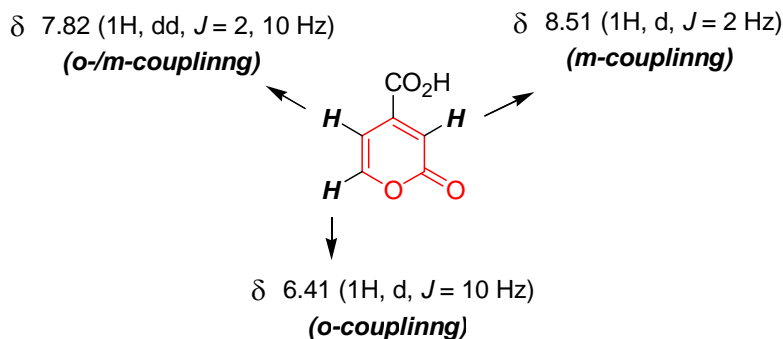
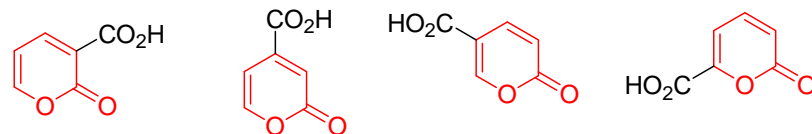


Answer:

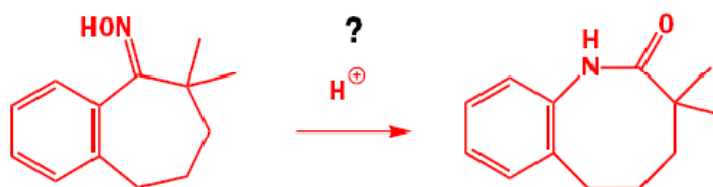


As observed in the ^1H -NMR spectrum, two methoxy protons resonate at 3.85 ppm i.e. the position of the methoxy groups in a ring such a way the molecule would be symmetric. In aromatic region, one proton resonates at 6.63 ppm and appeared as triplet with J value 2.0 Hz which implies meta-coupling. Two another aromatic protons appeared as doublet with the same J value (2.0 Hz) that clearly indicate again meta-coupling. Thus, among above three isomeric dimethoxybenzoic acids, the compound could be 3,5-dimethoxybenzoic acid.

Similarly,



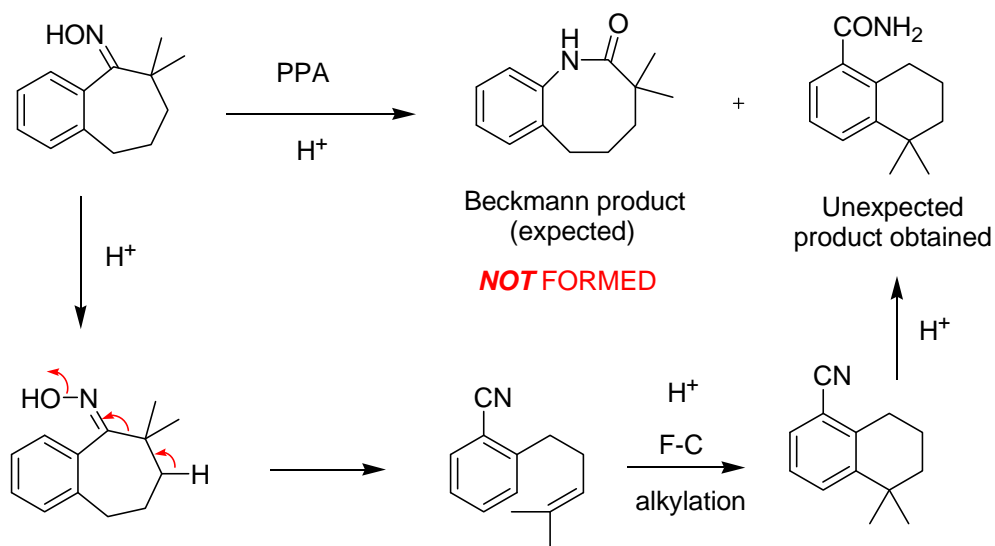
27. The reaction below was expected to give product A and did indeed give a product with the correct molecular formula by mass spectrometry. The ^1H NMR spectrum of the product was however: δ H (p.p.m.) 1.27 (6H, s), 1.70 (4H, m), 2.88 (2H, m), 5.4–6.1 (2H, broad s, exchanges with D_2O), 7.0–7.5 (3H, m). Though the detail is missing from this spectrum, how can you already tell that this is not the compound expected?



Answer:

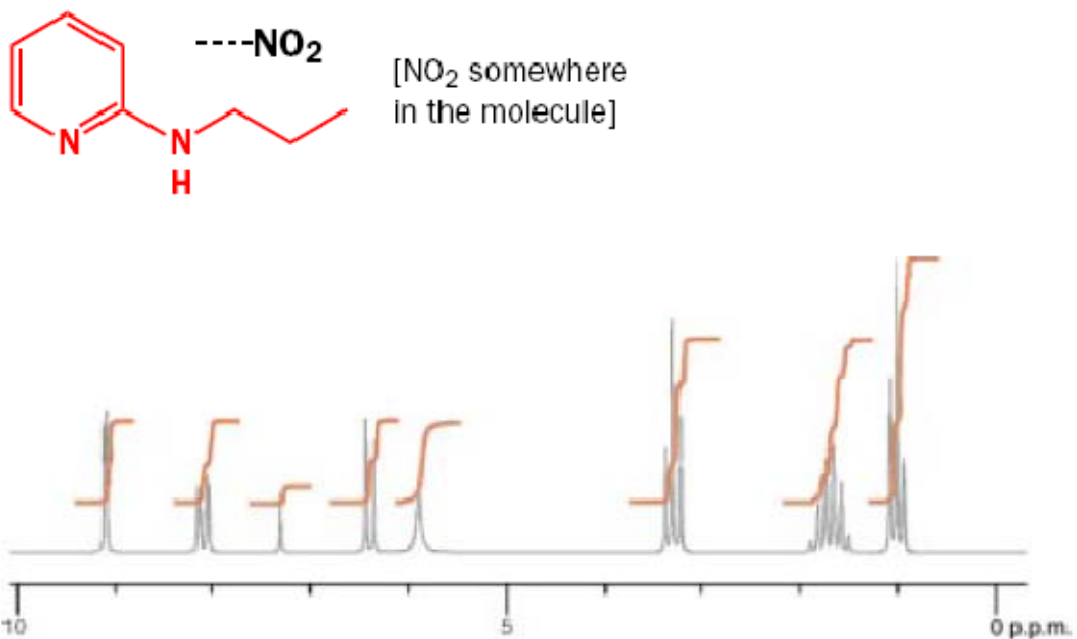
If you clinically analyze the product obtained through expected Beckmann rearrangement reaction condition, none of the protons resonate in lactams ring are fit. If we consider the expected ring expanded product as in the above scheme shown the lactams product should contain four aromatic protons, six methylene protons and one amide proton which might be exchangeable with D_2O . Actually, the ^1H NMR spectral data is completely mismatching with the expected one. Three aromatic protons resonate at [7.0–7.5 (3H, m)], two protons appeared as broad singlet [5.4–6.1 (2H, broad s, exchanges with D_2O)] which implies two amide [CONH_2]-protons. Therefore, one may consider to some other unexpected reaction occurred and give substituted tetralin product with amide functionality. The plausible reaction mechanism is depicted as follows:

Mechanism

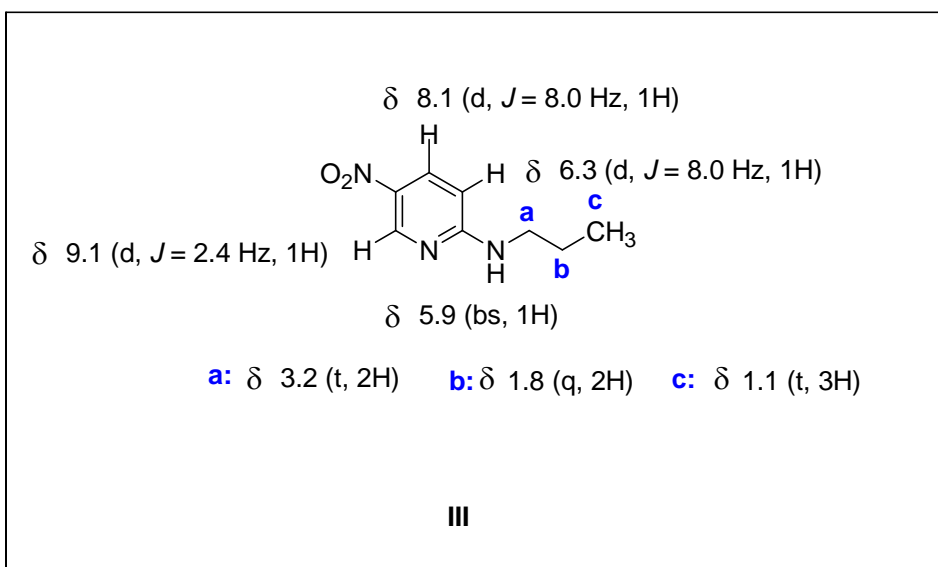


Now, you can correlate the ^1H NMR spectral data easily.

28. A nitration product ($C_8H_{11}N_3O_2$) of this pyridine has been isolated which has a nitro (NO_2) group somewhere on the molecule. From the 90 MHz 1H NMR spectrum, deduce whether the nitro group is (a) on the ring, (b) on the NH nitrogen atom, or (c) on the aliphatic side chain and then exactly where it is. Give a full analysis of the spectrum.

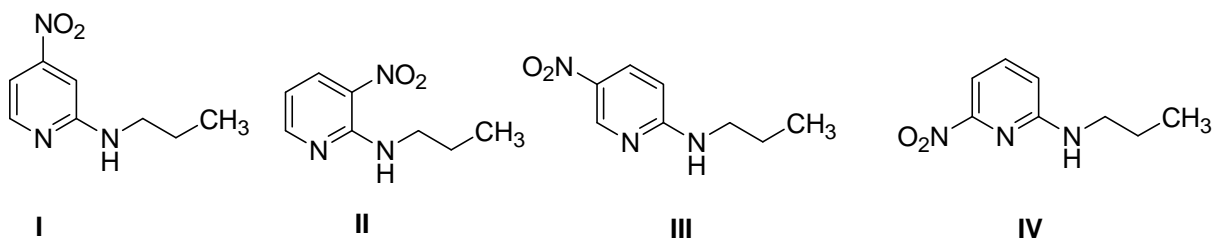


Answer:

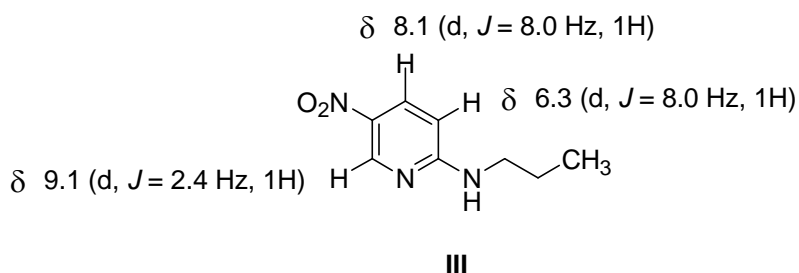


First Assumption (a)

If NO₂-group at aromatic region:

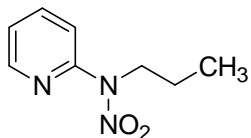


The most significant feature of the aromatic region is that one proton appeared at a very high downfield position about 9.1 ppm with *m*-coupling ($J = 2\text{--}3\text{ Hz}$) which rules out the isomer II and IV as no neighbours protons are there. Between I and III, all the protons most probably fit well with the isomer III and the value is designated for all the protons as below:



Second Assumption (b)

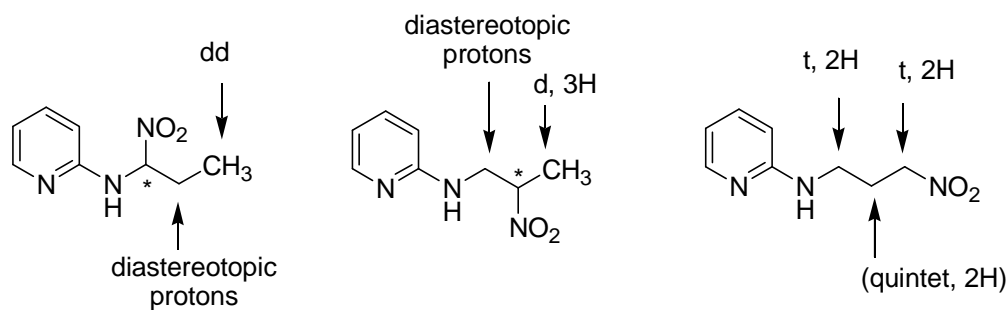
If NO₂-group is attached with N



In ¹H NMR spectra as shown above the chemical shift value δ 5.9 ppm is typical for NH proton so it is free NH.

Third Assumption (c):

If NO₂-group is at propyl chain

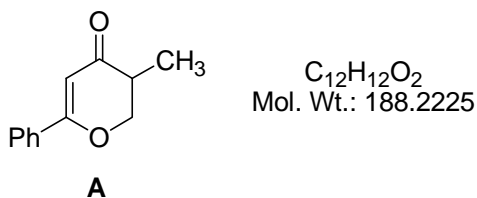


All the above estimated spectral analysis is not exactly matching with the above spectral data. Thus -NO₂ group is not attached with side propyl chain, it is attached with aromatic carbon.

29. The natural product bullatenone was isolated in the 1950s from a New Zealand myrtle and assigned the structure **A**. Then compound **A** was synthesized and found not to be identical with natural bullatenone. Predict the expected ^1H NMR spectrum of **A**. Given the full spectroscopic data available nowadays, but not in the 1950s, say why **A** is definitely wrong and suggest a better structure for bullatenone.

Spectra of bullatenone:

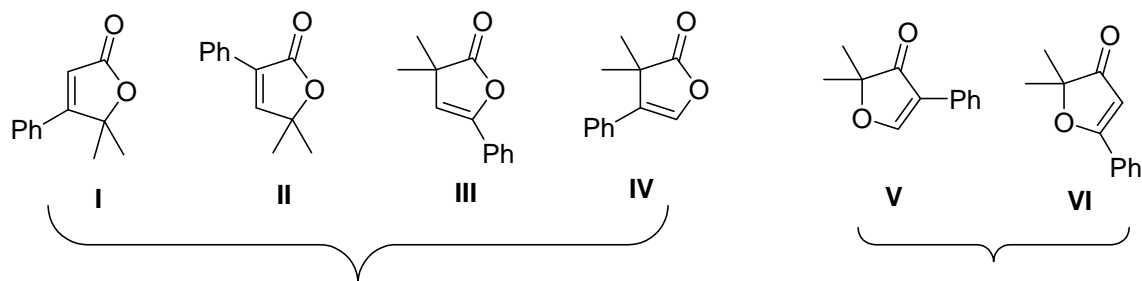
Mass spectrum: m/z 188 (10%) (High resolution confirms $\text{C}_{12}\text{H}_{12}\text{O}_2$), 105 (20%), 102 (100%), and 77 (20%) Infrared: 1604 and 1705 cm^{-1} . ^1H NMR: 1.45 (6H, s), 5.82 (1H, s), 7.35 (3H, m), and 7.68 (2H, m).



Answer:

Mid 20th century, the chemists were faced a tremendous problem to deduce the structure of any unknown compound that could be extracted from natural plants. The IR and mass spectra of above structure (A) are possibly matching. Later, after synthesizing the proposed compound and once the NMR spectra had taken, it was found that the proposed structure of A, natural bullatenone is completely wrong. Thus later the structure is revisited and it's true that simple using NMR techniques this above problem can be solved.

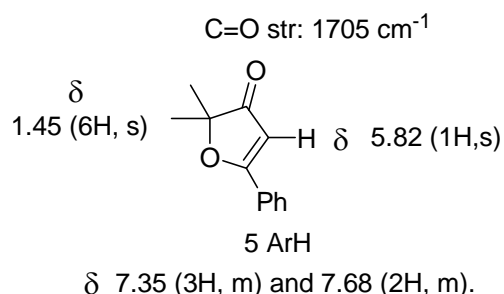
In the ^1H NMR spectral analysis it is found that the compound has five aromatic protons (ArH), six methyl protons (CMe_2) and one olefin proton at normal olefin region. Again, the analysis of IR spectra clearly indicates one carbonyl group ($\text{C}=\text{O}$) so if we add together the molecular formula would be $\text{C}_{12}\text{H}_{12}\text{O}$. Oxygen is short. It is expected that one more oxygen might be in the ring. So the probable structure would be as follows:



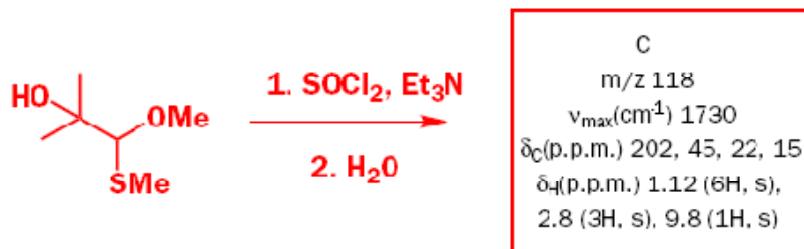
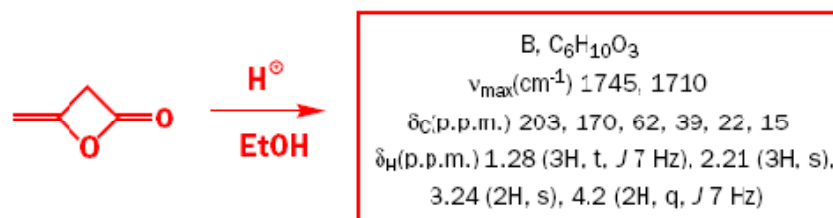
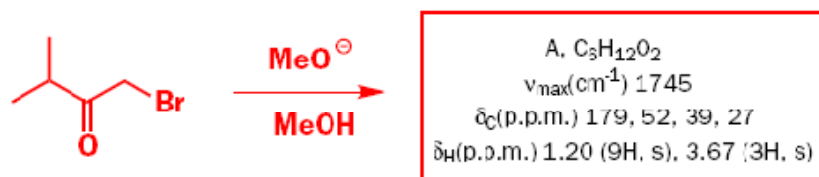
Lactone (I to IV) could not be:

- Lactone carbonyl carbon stretching frequency would be $\sim 1745\text{-}1780\text{ cm}^{-1}$, although in the structures I and II, there is a double bond in conjugation with carbonyl group still it never came at 1705 cm^{-1} .
- In the structure IV, the alkene proton must be appeared at higher chemical shift value than normal olefin region.

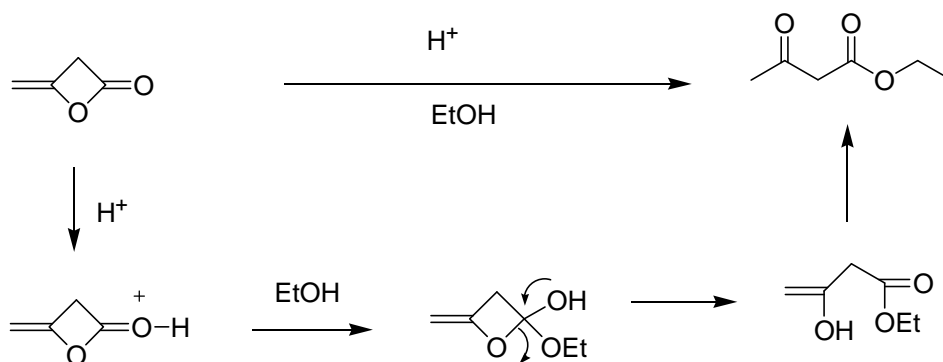
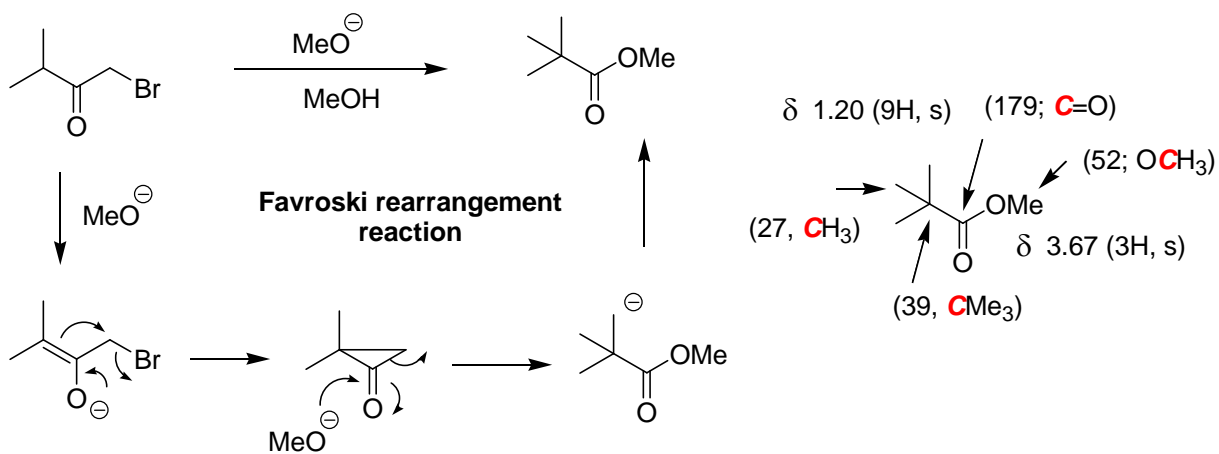
Between V and VI, the corrected structure could be VI. All the spectroscopic data is fit.



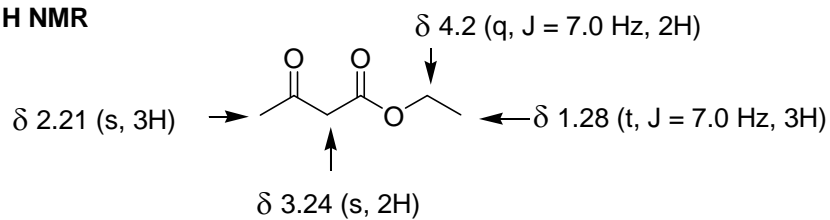
30. Suggest structures for the products of these reactions, interpreting the spectroscopic data.



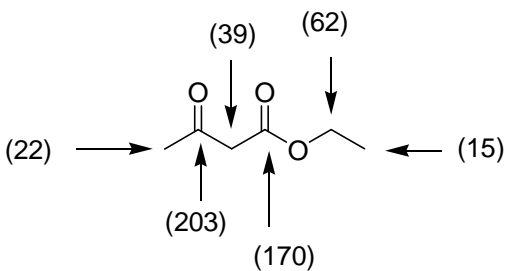
Answer:



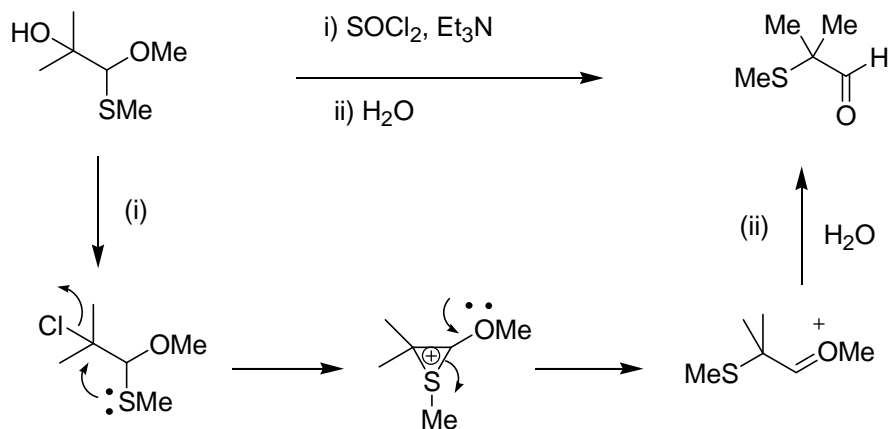
¹H NMR



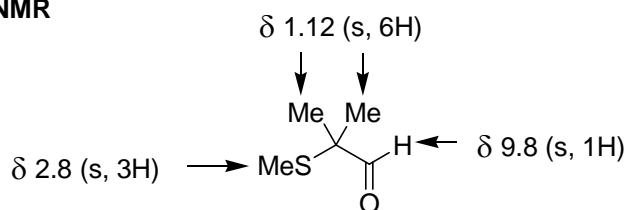
¹³C NMR



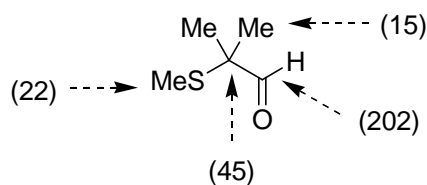
C=O str: 1705 cm⁻¹



¹H NMR



¹³C NMR



31. Precocene is an organic compound that causes insect larvae to pupate and can also be found in some plants (*Ageratum* spp.) where it may act as an insecticide. It was isolated in minute amounts and has the following spectroscopic details. Propose a structure for precocene.

Spectra of precocene:

Mass spectrum: m/z (high resolution gives C₁₃H₁₆O₃), M—15 (100%) and M—30 (weak).

Infrared: CH and fingerprint only.

¹H NMR: 1.34 (6H, s), 3.80 (3H, s), 3.82 (3H, s), 5.54 (1H, d, *J* = 10 Hz), 6.37 (1H, d, *J* = 10 Hz), 6.42 (1H, s), and 6.58 (1H, s).

Answer:

DBEs = 6

Mass spectrum: $M-15$ (100%); Methyl group easily fragmented from the molecule.

Infra red spectra: Only the peaks of CH and fingerprint only which clearly suggest that all the three oxygens are in ether linkages. No carbonyl functionality is present in the molecule.

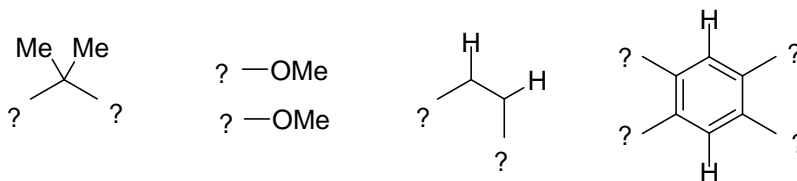
$^1\text{H NMR}$: 1.34 (6H, s) —Two set of methyl protons (Chemically equivalent; probably $-\text{CMe}_2$)

3.80 (3H, s), 3.82 (3H, s) —Two set of methoxy protons ($-\text{OMe}$) attached

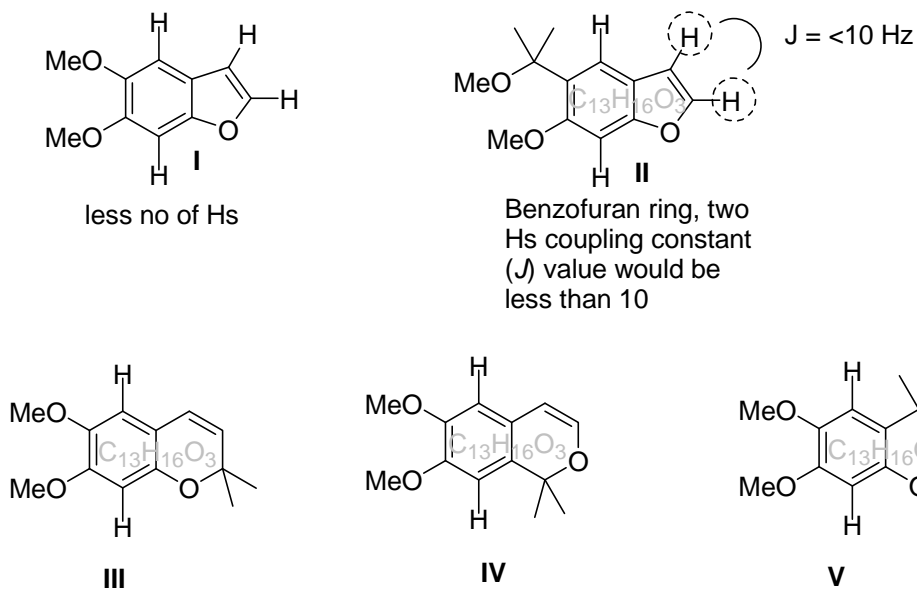
5.54 (1H, d, $J = 10$ Hz), 6.37 (1H, d, $J = 10$ Hz) —Suggest two olefin protons and their relationship is *cis*-to each other.

6.42 (1H, s), and 6.58 (1H, s) —clarify two aromatic protons attached in a 1,4-position and appeared as a singlet. There are no neighbouring protons are there.

Thus the fragments are as follows:

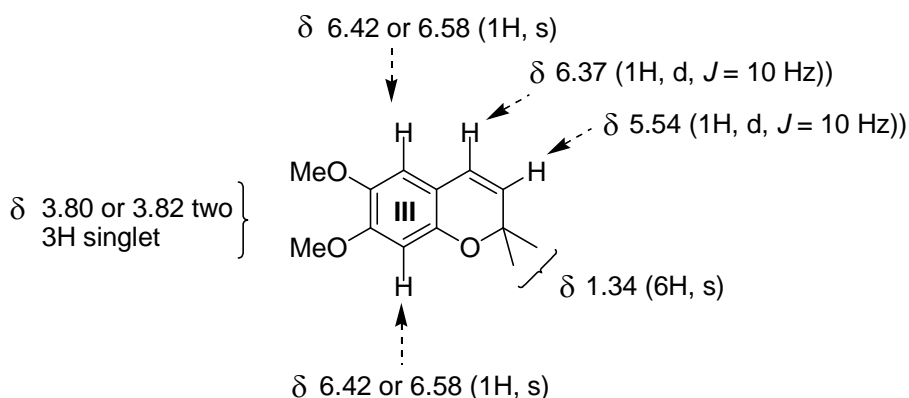


If we connect all these above fragments, the following structures would be possible:



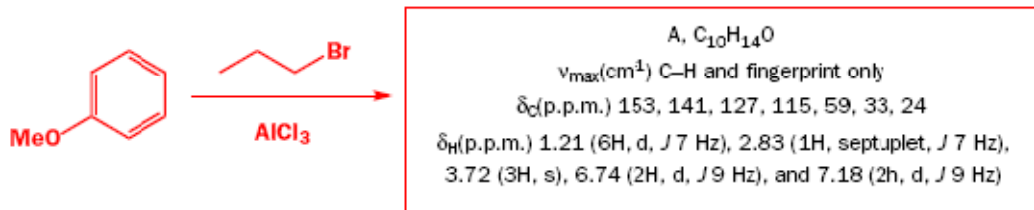
As suggested before the possible structures, structure **I** and **II** would not be possible as five membered ring systems, the protons coupling constants would be small, never would be 10 Hz. Thus these structures rule out. The other six-membered heterocycles (**III**, **IV** and **V**), the structures **IV** and **V** again would not be possible as the olefin hydrogen connected with oxygen resonate at higher chemical shift value and of course, there would be a substantial chemical shift differences were observed between two olefin Hs.

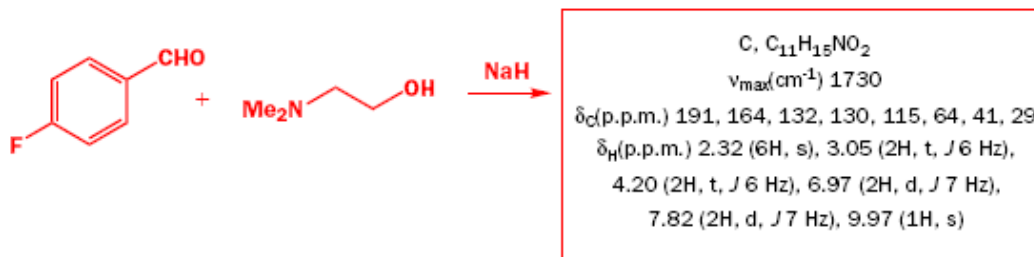
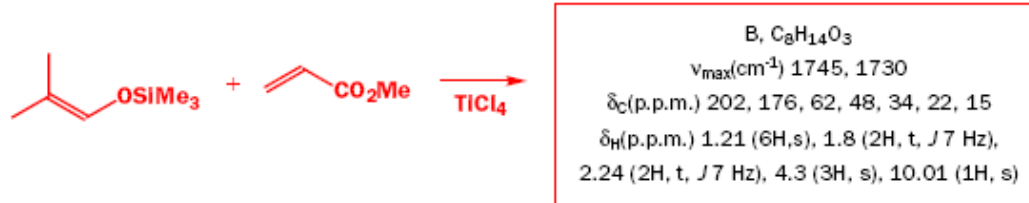
Thus only left the structure no **III**, which fits all the spectroscopic data which is represented as follows:



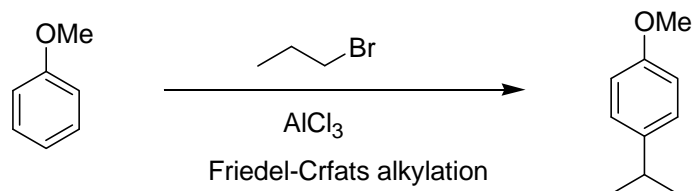
DBEs = 6 (4 double bonds and two rings)
 Mass: M-15 is possible
 IR: only C-H and fingerprint region, as no characteristic functional groups are present.
 ^1H NMR: Best fit as observed.

32. Suggest structures for the products of these reactions, interpreting the spectroscopic data.

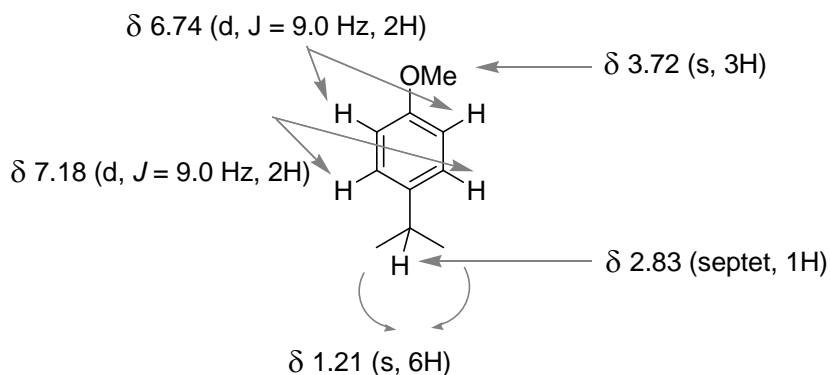




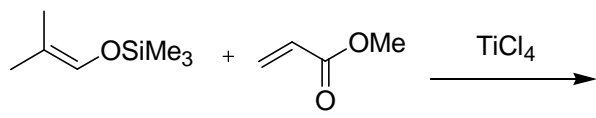
Answer:
(Solution I)



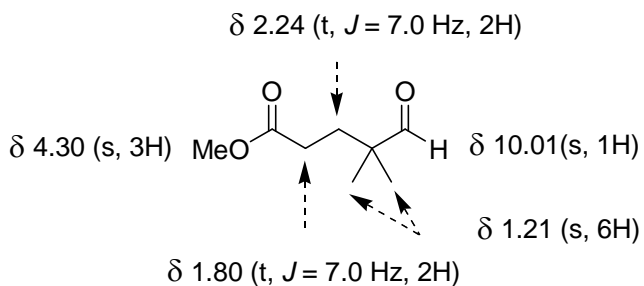
This is a traditional Friedel-Crafts alkylation reaction. In the IR spectral analysis, it is observed that no as such characteristic functional groups are present except C-H stretching frequency and the peaks at fingerprint region. In ¹H-NMR spectrum, two methyl protons resonate at δ value 1.21 ppm as a singlet which implies $-\text{CHMe}_2$, one proton appeared as septet at δ value 2.83 ppm i.e. presence of methane proton and attached with a six neighbouring protons. One methoxy group is there (at 3.72 ppm) and four aromatic protons are present. Two pair of doublet at δ values 6.74 ppm and 7.18 with equal *ortho*-coupling pattern indicating the substitution pattern is 1,4-disubstituted.



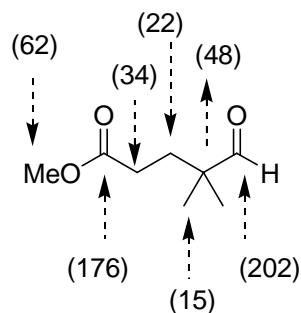
(Solution II)



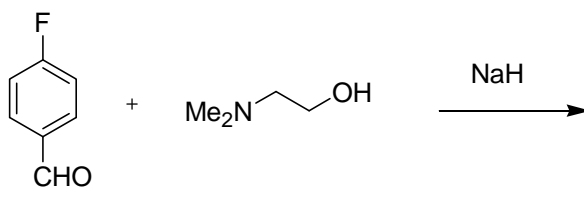
¹H NMR



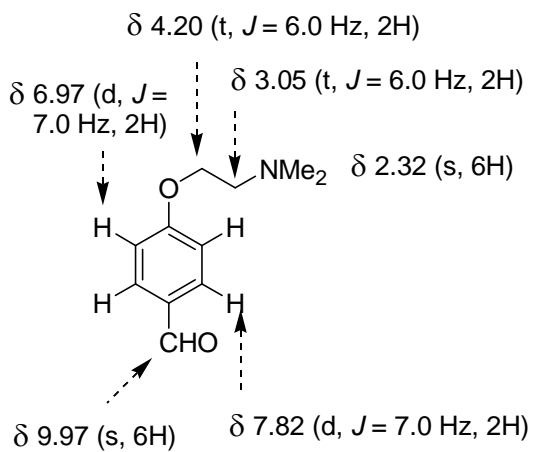
¹³C NMR



(Solution III)



¹H NMR



¹³C NMR

