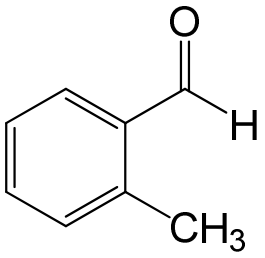
WORKSHEET I_Keys

1. Predict the positions of the major absorption bands in the IR spectra of the following compounds

A



$\ddot{\upsilon}_{C\text{-}HAr}$ = 3100 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

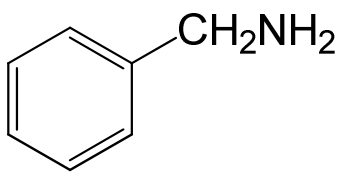
$\ddot{\upsilon}_{C\text{-}HAldehyde}$ = 2880, 2700 cm^{-1}

$\ddot{\upsilon}_{C=O}$ = 1680 cm^{-1}

$\ddot{\upsilon}_{C=C\_Ar}$ = 1600,1450 cm^{-1}

$\ddot{\upsilon}_{C\text{-}HAr\_ben}$ = 600 - 800 cm^{-1}

B



$\ddot{\upsilon}_{NH2}$ = 3300 and 3250 cm^{-1}

$\ddot{\upsilon}_{C\text{-}HAr}$ = 3100 cm^{-1}

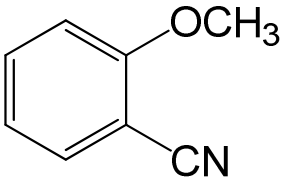
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

$\ddot{\upsilon}_{C=C\_Ar}$ = 1600, 1450 cm^{-1}

$\ddot{\upsilon}_{C\text{-}N}$ = 1100 cm^{-1}

$\ddot{\upsilon}_{C\text{-}HAr\_ben}$ = 600 - 800 cm^{-1}

C



$\ddot{\upsilon}_{C\text{-}HAr}$ = 3100 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

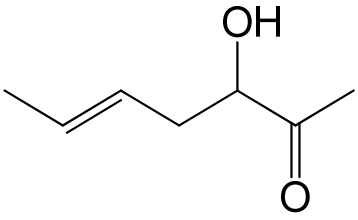
$\ddot{\upsilon}_{CN}$ = 2210 cm^{-1}

$\ddot{\upsilon}_{C=C\_Ar}$ = 1600, 1450 cm^{-1}

$\ddot{\upsilon}_{C\text{-}O}$ = 1100 cm^{-1}

$\ddot{\upsilon}_{C\text{-}HAr\_ben}$ = 600 - 800 cm^{-1}

D



$\ddot{\upsilon}_{OH}$ = 3200 - 3300 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp2}$ = 3100 cm^{-1}

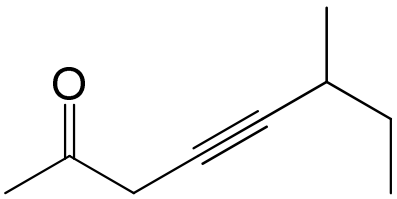
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

$\ddot{\upsilon}_{C=O}$ = 1720 cm^{-1}

$\ddot{\upsilon}_{C=C}$ = 1650 cm^{-1}

$\ddot{\upsilon}_{C\text{-}O}$ = 1100 cm^{-1}

E

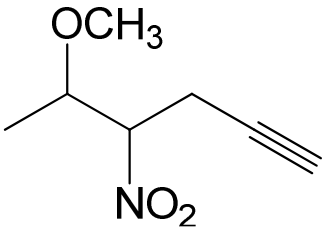


$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

$\ddot{\upsilon}_{CC\_triple\_bond}$ = 2220 cm^{-1}

$\ddot{\upsilon}_{C=O}$ = 1720 cm^{-1}

F



$\ddot{\upsilon}_{C\text{-}Hsp}$ = 3300 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

$\ddot{\upsilon}_{CC\_triple\_bond}$ = 2220 cm^{-1}

$\ddot{\upsilon}_{NO2}$ = 1520 and 1330 cm^{-1}

$\ddot{\upsilon}_{C\text{-}O}$ = 1100 cm^{-1}

2. Which compound would be expected to show intense IR absorption at 3300 cm^{-1}?
A) $CH_3C{\equiv}CCH_3$ B) butane C) but-1-ene D) $CH_3CH_2C{\equiv}CH$

Only D can show a C-Hsp signals around 3300 cm^{-1}

3. Which compound would be expected to show intense IR absorption at 2820, 2710 and 1705 cm^{-1}?
A) $CH_3COCH_2CH_3$ B) $PhCOCH_3$ C) PhCHO D) $CH_2{=}CHCOCH_3$

Only C can show the signals corresponding to the C-H of aldehyde at 2820, 2710 and 1705 cm^{-1}

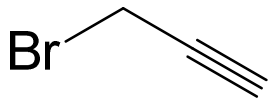
4. Which compound would be expected to show intense IR absorption at 2250 cm^{-1}?
A) $CH_3CH_2CH_2CO_2H$ B) $(CH_3)_2CHCH_2OH$ C) $(CH_3)_2CHCN$ D) $CH_3CH_2CH_2CONH_2$

Only C can show a signal corresponding to the CN triple bond around 2250 cm^{-1}

5. Deduce a possible structure for the following compounds from their IR absorptions below.

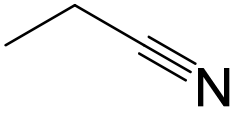
A

C_3H_3Br: 3300, 2900, 2100 cm^{-1}, NI = 3 + 1 – ½ x 4 = 2 elements of insaturations which correspond to a CC triple bond around 2100 cm^{-1} and C-Hsp at 3300 cm^{-1}. The last signal is that of $CHsp^3$ at 2900 cm^{-1}, leading to the structure below.



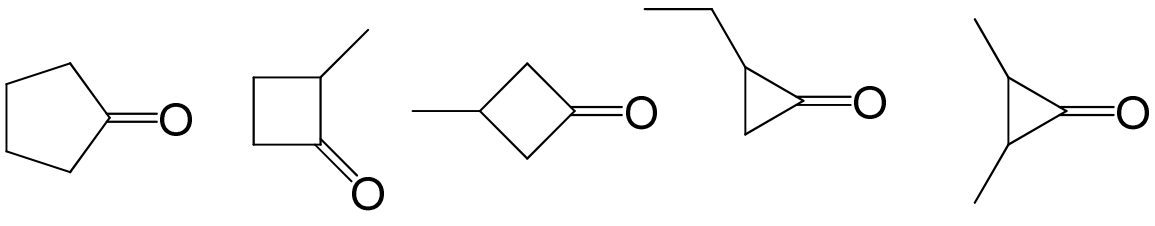
B

C_3H_5N: 2950, 2250 cm^{-1}, NI = 3 + 1 – ½ x 5 + ½ = 2 elements of insaturations which correspond to the nitrile functional group, and the last signal is that of $CHsp^3$ at at 2950 cm^{-1}, leading to the structure below.



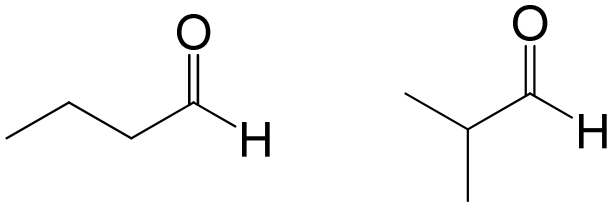
C

C_5H_8O: 2950, 1750 cm^{-1}, NI = 5 + 1 – ½ x 8 = 2 elements of insaturations, one of which correspond to the carbonyl group (C=O at 1750 cm^{-1}), the other to a ring system, since the last signal is that of $CHsp^3$. The following structures are consitent with the IR data.



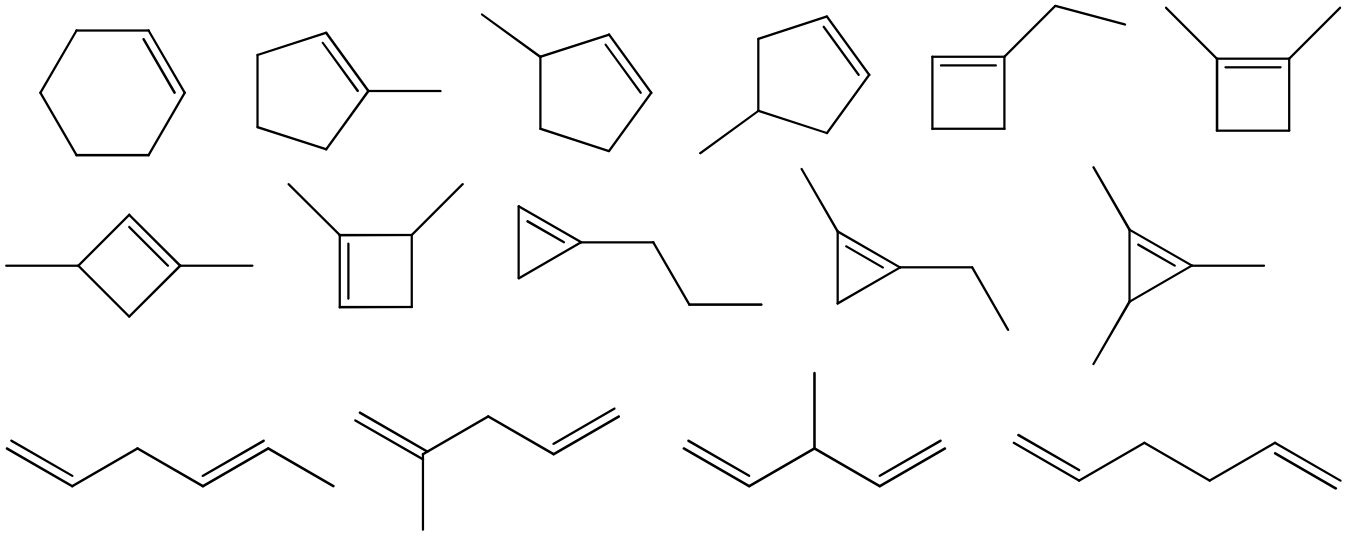
D

C_4H_8O: 2950, 2820, 2715, 1715 cm^{-1}, NI = 4 + 1 – ½ x 8 = 1 elements of insaturation, corresponding to the aldehyde functional group (2820, 2715 and 1715 cm^{-1}). The last signal is that of $CHsp^3$. The following structures are consitent with the IR data.



E

C_6H_{10}: 3040, 2980, 1660 cm^{-1}, NI = 6 + 1 – ½ x 10 = 2 elements of insaturation, corresponding to the C-Hsp^2 at 3040 cm^{-1}, C-Hsp^3 at 2980 cm^{-1}, and C=C at 1660 cm^{-1}. The following structures are consitent with the IR data.



6. How could IR spectroscopy be used to distinguish between the following pair of compounds? You should also list all the major absorption bands in the IR spectra of each of compound.

A $CH_3OCH_2CH_3$ and $CH_3CH_2CH_2OH$

$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C\text{-}O}$ = 1100 cm^{-1}

$\ddot{\upsilon}_{OH}$ = 3200 - 3300 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C\text{-}O}$ = 1100 cm^{-1}

The only difference is that the alcohol will display a broad signal for the OH while the ether will not.

B $HOCH_2CH_2CHO$ and $CH_3CH_2CO_2H$

$\ddot{\upsilon}_{OH}$ = 3200 - 3300 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C\text{-}H\_aldehyde}$ = 2820 and 2750 cm^{-1}
$\ddot{\upsilon}_{C=O}$ = 1750 cm^{-1}
$\ddot{\upsilon}_{C\text{-}O}$ = 1100 cm^{-1}

$\ddot{\upsilon}_{OH}$ = 2500 - 3400 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C=O}$ = 1720 cm^{-1}

The carboxylic acid will show a broader OH signal then that of the alcohol, but compound 1 will also show characteristic signals of aldehyde that will be absent in the IR of compound 2.

C $CH_3COCH{=}CHCH_2CH_3$ and $CH_3COCH_2CH_2CH{=}CH_2$

$\ddot{\upsilon}_{C\text{-}Hsp2}$ = 3100 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C=O}$ = 1680 cm^{-1}
$\ddot{\upsilon}_{C=C}$ = 1600 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp2}$ = 3100 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C=O}$ = 1750 cm^{-1}
$\ddot{\upsilon}_{C=C}$ = 1620 cm^{-1}

Both compounds will display almost the same signals with the difference that in compound 1, the two double bonds are conjugated, resulting in lower IR signals as compared to compound 2 in which the double bonds are isolated from each other.

D $CH_3CH_2C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$

$\ddot{\upsilon}_{C\text{-}Hsp}$ = 3300 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{CC\_triple\ bond}$ = 2200 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

In addition to the signal of $CHsp^3$, only compound 1 will show the signals related to the CC triple bond and C-Hsp, while compound 2 will only show a signal for $CHsp^3$, because of the lack of a change in the dipole moment.

E $CH_2{=}CHCH_2CH(CH_3)_2$ and $CH_3CH_2CH_2CH(CH_3)_2$

$\ddot{\upsilon}_{C\text{-}Hsp2}$ = 3100 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C=C}$ = 1650 cm^{-1}

$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}

Compound 1 will show, in addition to the signal for $CHsp^3$, signal related to $CHsp^2$ and C=C, while compound will display only the signal related to $CHsp^3$.

7. Ethyne (HC≡CH) does not show IR absorption in the region 2000-2500 cm^{-1} because:

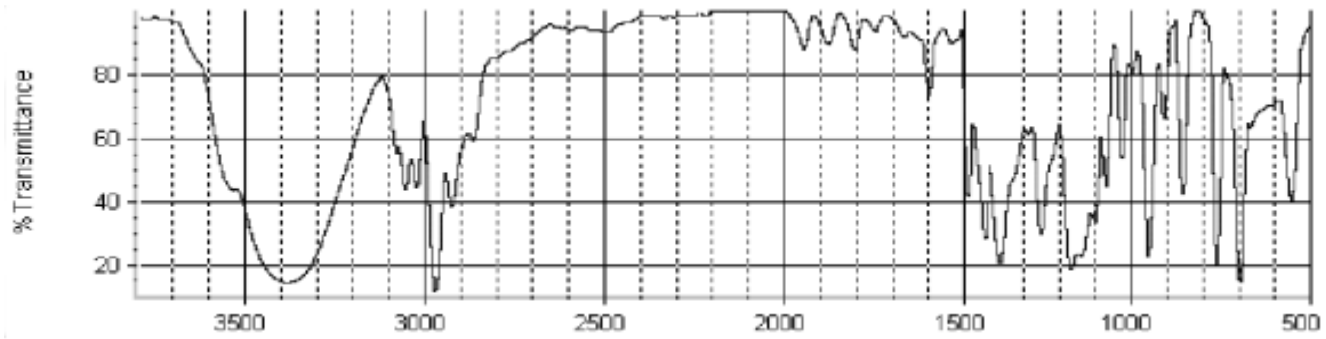
A) C–H stretches occur at lower energies.

B) C≡C stretches occur at about 1640 cm^{-1}.

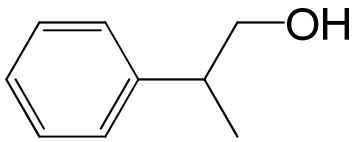
C) there is no change in the dipole moment when the C≡C bond in ethyne stretches.

D) there is a change in the dipole moment when the C≡C bond in ethyne stretches.

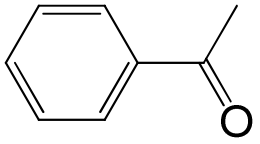
8. Which of the following structures is consistent with the IR spectra shown below?



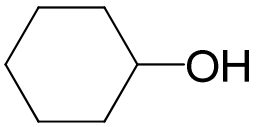
A



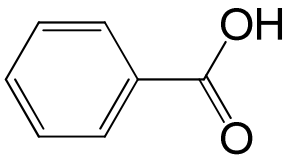
B



C

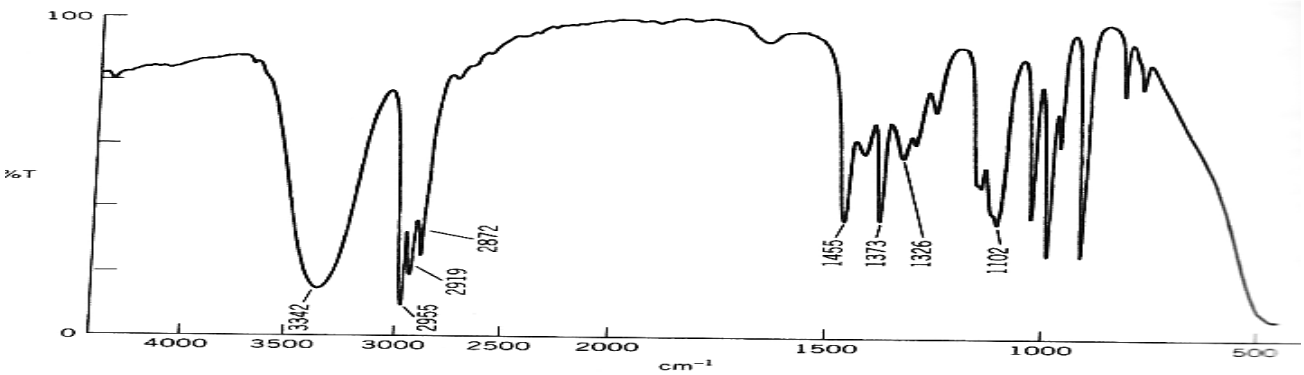


D

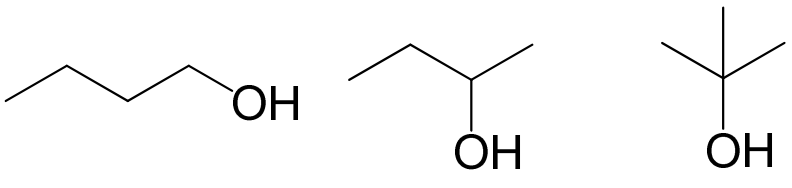


Only A displays, in addition to the signal of OH alcohol, characteristic signal of the aromatic ring. C cannot show the aromatic characteristics, B cannot show an OH signal, while D will display a much broader OH signal due to the carboxylic acid.

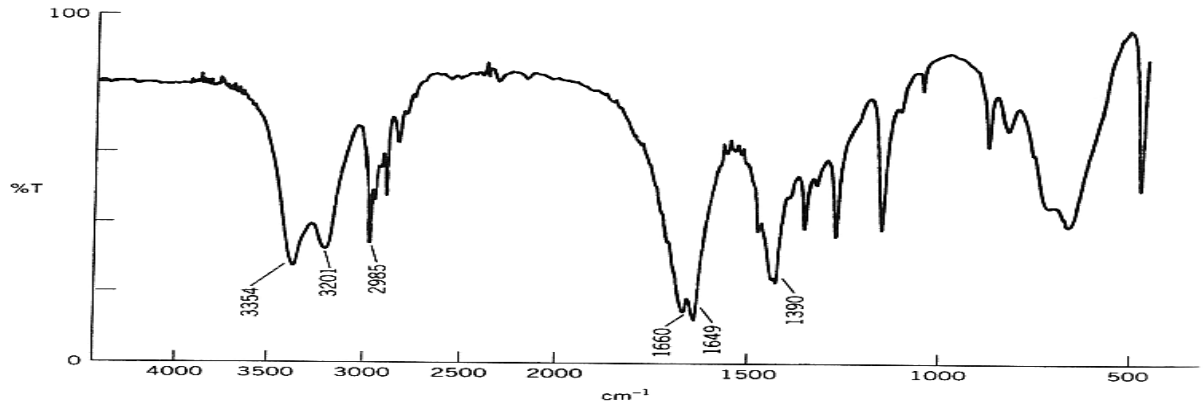
9. Explain which functional group(s) is present in the compound that has the following IR spectra
The molecular formula is $C_4H_{10}O$



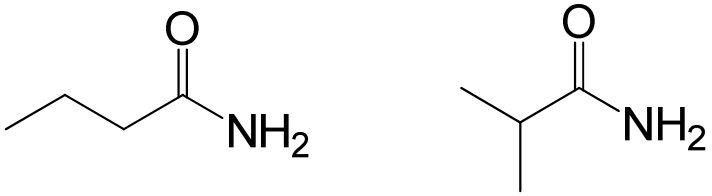
NI = 4 + 1 – ½ 10 = 0. There is no insaturation and the molecule shows a signal of OH alcohol and of CHsp^3, characteristic of saturated alcohols.



10. Explain which functional group(s) is present in the compound that has the following IR spectra The molecular formula is C_4H_9NO



NI = 4 + 1 – ½ 9 + ½ = 1. The insaturation corresponds to the carbonyl at 1660-1649 cm^{-1}. The molecule also shows a bidented signal of NH_2 of amide, as well as a signal of CHsp^3, characteristic of saturated and unsubstituted amide.



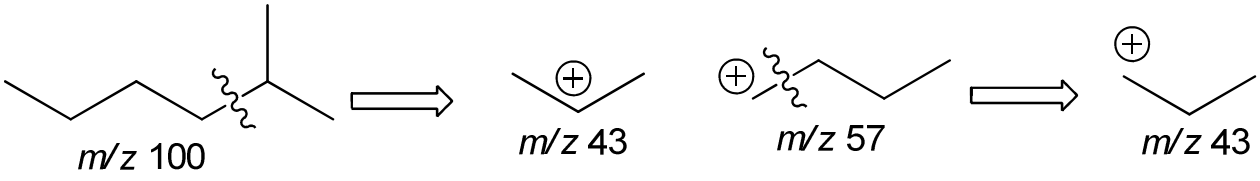
11. Which compound would be expected to show intense IR absorption at 1715 cm^{-1}?
A) $(CH_3)_2CHNH_2$ B) hex-1-yne C) 2-methylhexane **D) $(CH_3)_2CHCO_2H$**

Only D can show a signal related to a carbonyl

12. Which compound would be expected to show intense IR absorption at 3363, 3185, 1660 cm^{-1}?
A) $CH_3CH_2CH_2OH$ B) $(CH_3)_2CHNH_2$ **C) $CH_3CH_2CONH_2$** D) but-1-ene

Only C can show a signal related to a carbonyl and to an amide

13. 2-Methylhexane shows an intense peak in the mass spectrum at *m/z* = 43. Propose a likely structure for this fragment.

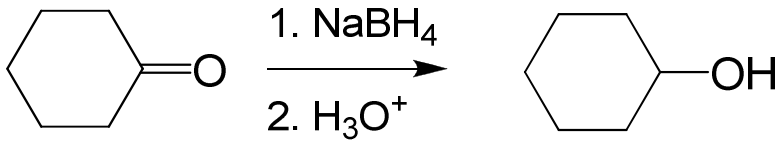


14. Which compound would show a larger than usual M+2 peak in the mass spectrum?

A) $CH_3CH_2SCH_3$ B) $(CH_3)_2CHNH_2$ C) $CH_3CH_2CO_2H$ D) $CH_3(CH_2)_2CH_3$

Only compound A has an atom with two isotopes at M and M + 2, namely sulfur

15. Sodium borohydride can be used to reduce cyclohexanone to cyclohexanol. How could one use IR to determine if all starting material had been consumed?



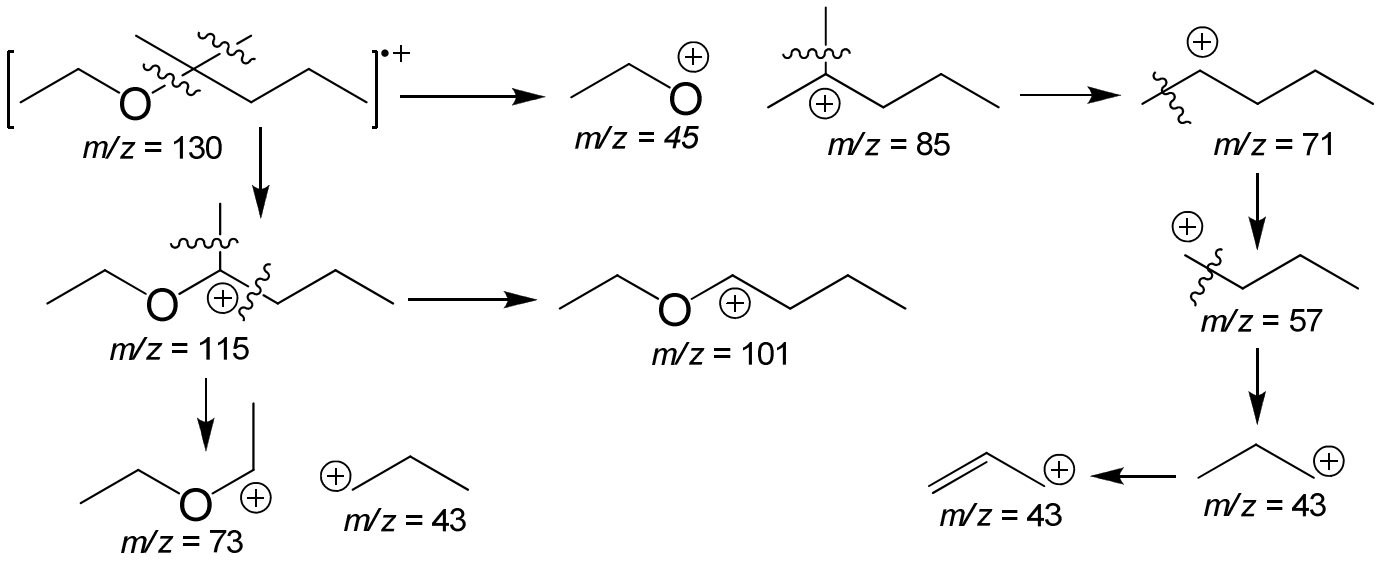
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C=O}$ = 1750 cm^{-1}

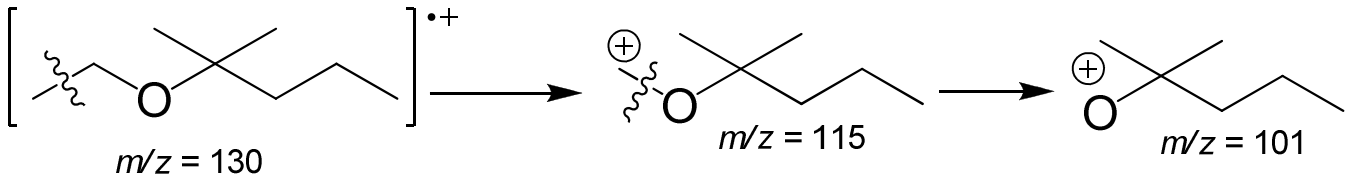
$\ddot{\upsilon}_{OH}$ = 3200 -3500 cm^{-1}
$\ddot{\upsilon}_{C\text{-}Hsp3}$ = 2950 cm^{-1}
$\ddot{\upsilon}_{C\text{-}O}$ = 1150 cm^{-1}

If all the starting material is consumed, the IR will not display any signal of C=O and instead will display a signal of a broad OH between 3200 – 3500 cm^{-1}.

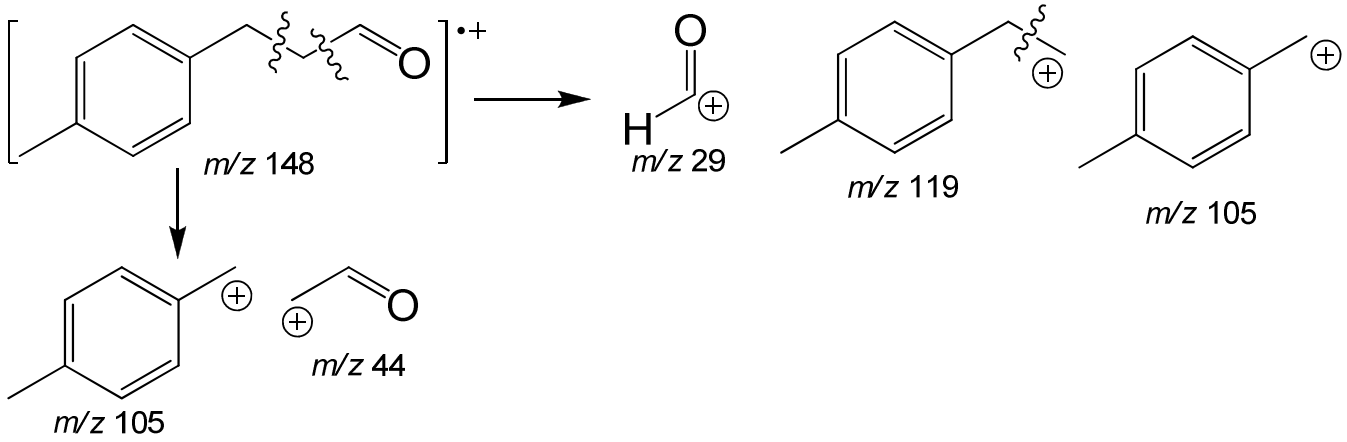
16. Predict the major fragments and their *m/z* that would appear in the mass spectra of these compounds:

A

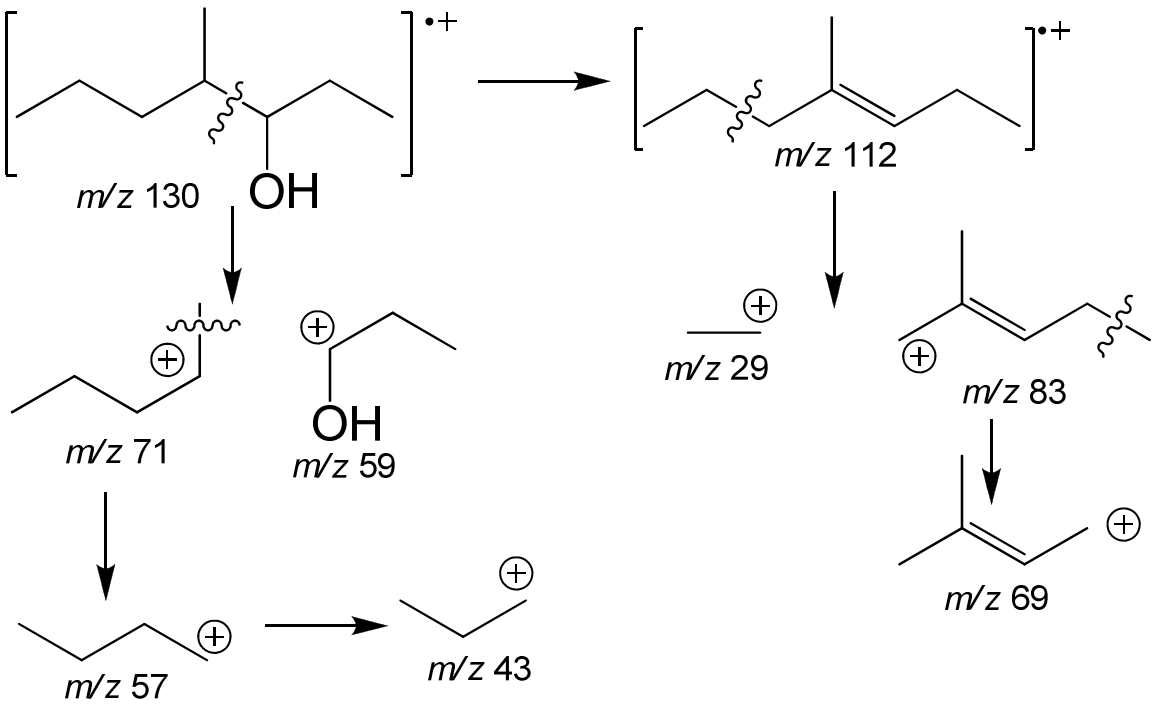




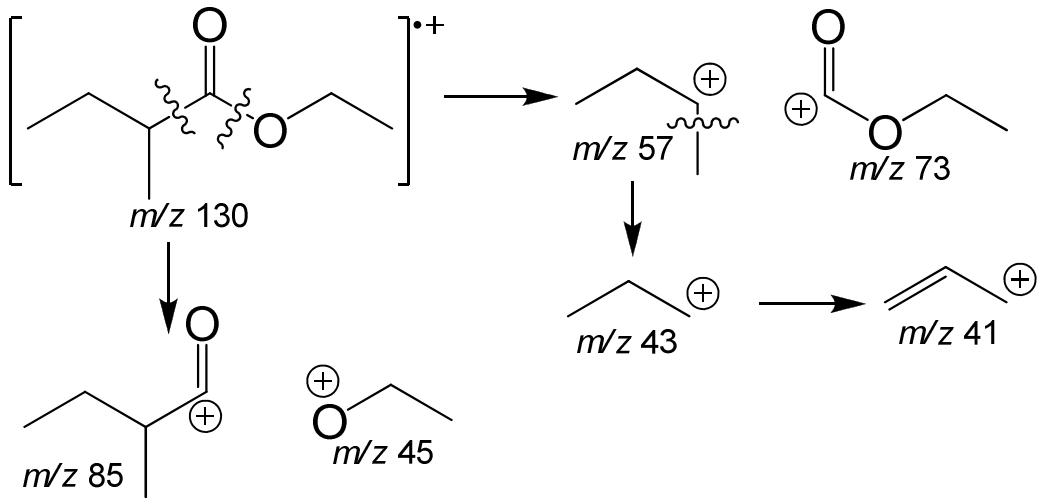
B

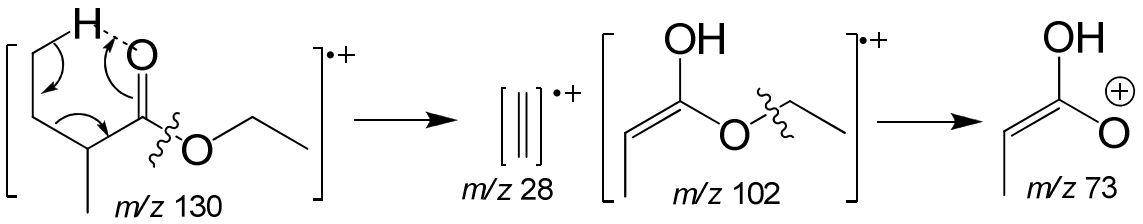

m/z 148
m/z 29
m/z 119
m/z 105
m/z 105
m/z 44

C

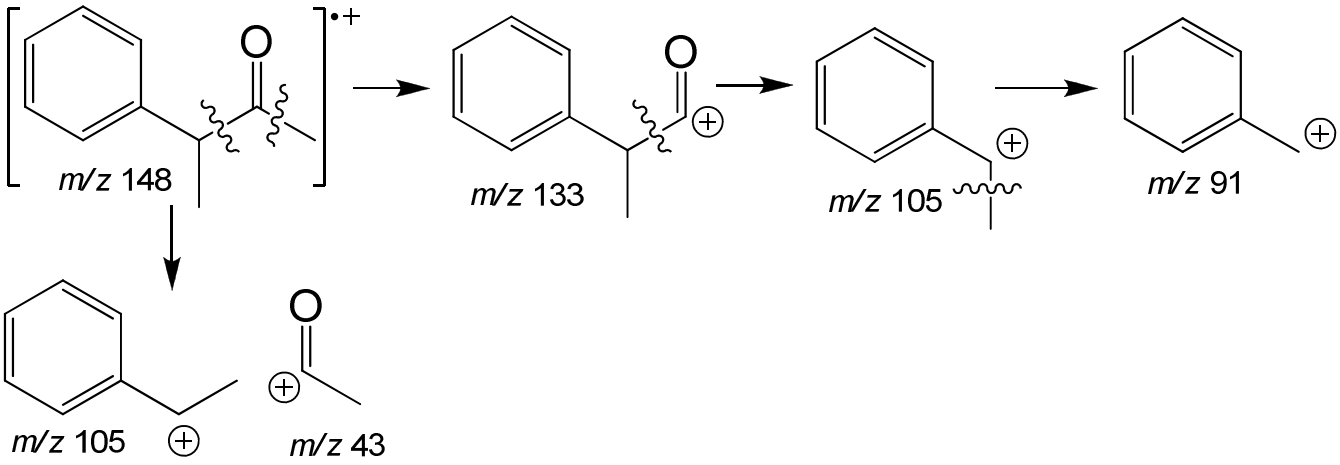

m/z 130
OH
m/z 112
m/z 71
OH
m/z 59
m/z 29
m/z 83
m/z 69
m/z 57
m/z 43

D

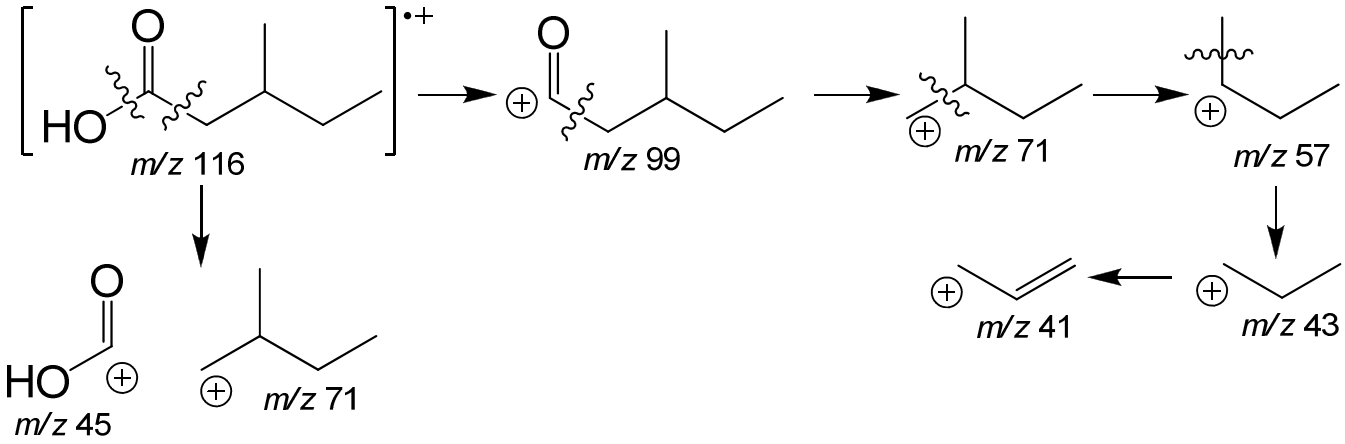

m/z 130
m/z 57
m/z 73
m/z 43
m/z 41
m/z 85
m/z 45

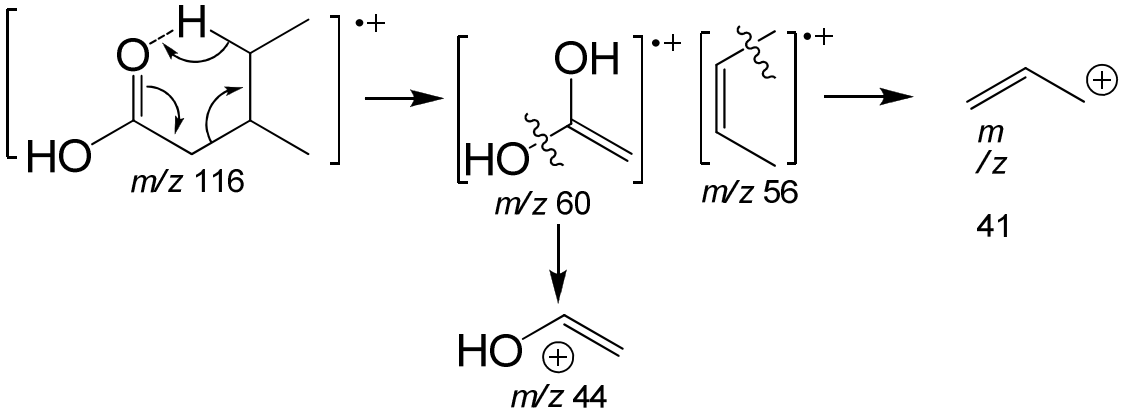

H
O
O
m/z 130
m/z 28
OH
O
m/z 102
OH
O
m/z 73

E


O
m/z 148
m/z 133
m/z 105
m/z 91
m/z 105
O
m/z 43

F


O
HO
m/z 116
m/z 99
m/z 71
m/z 57
m/z 41
m/z 43
O
HO
m/z 45
m/z 71


H
O
HO
m/z 116
OH
HO
m/z 60
m/z 56
m
/z
41
HO
m/z 44

17. (a) Both $C_6H_{10}O$ and C_7H_{14} have the same nominal mass, namely 98. Show how these compounds can be distinguished by the *m/z* ratio of their molecular ions in high-resolution mass spectrometry.

At high resolution, the mass is given with more significant digits, enabling to distinguish between compounds with close molecular masses

$C_6H_{10}O$ = 6 x 12.011 + 10 x 1.0079 + 15.999 = 98.144

C_7H_{14} = 7 x 12.011 + 14 x 1.0079 = 98.1876

98.1876 – 98.144 = 0.0436

Although both compounds have a nominal mass of 98, at high resolution they are different by 0.0436.

b) same question for C_6H_9N and C_5H_5NO.

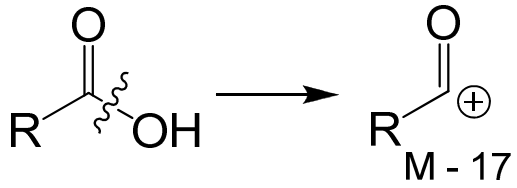
C_6H_9N = 6 x 12.011 + 9 x 1.0079 + 14.007 = 95.1441

C_5H_5NO = 5 x 12.011 + 5 x 1.0079 + 15.999 + 14.007 = 95.1005

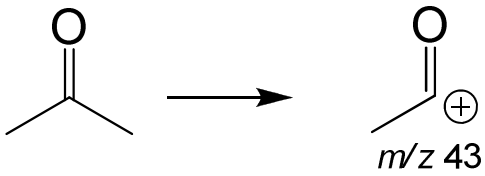
95.1441 – 95.1005 = 0.0436

Although both compounds have a nominal mass of 95, at high resolution they are different by 0.0436.

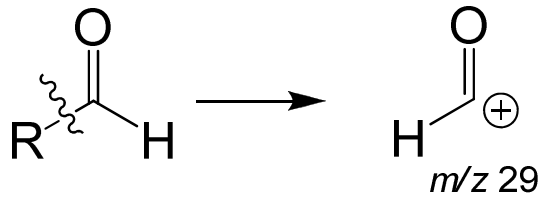
18. Carboxylic acids often give a strong fragment ion at *m/z* (M-17). What is the likely structure of this cation? Show by drawing contributing structures that it stabilized by resonance.



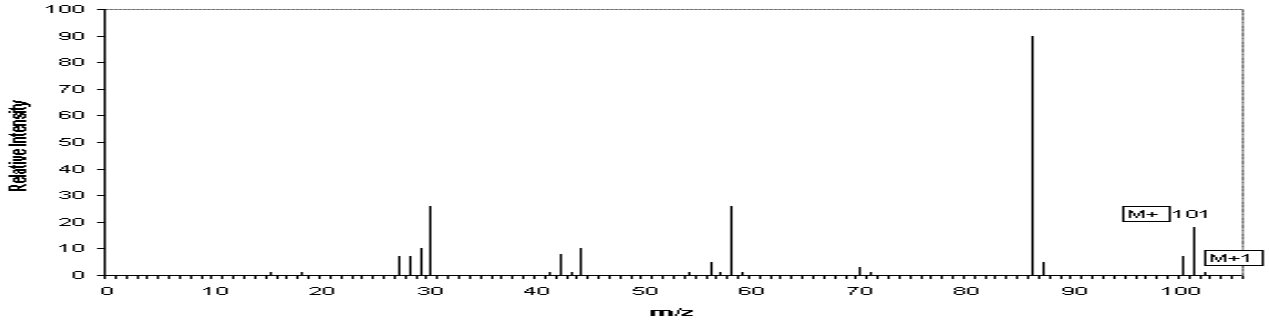
19. The base peak in the mass spectrum of propanone (acetone) occurs at *m/z* 43. What cation does this peak represents?

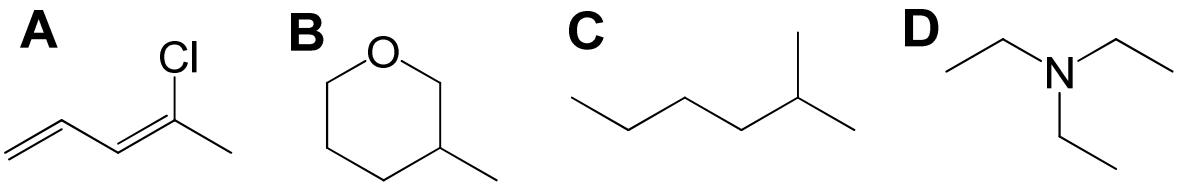


20. A characteristic peak in the mass spectrum of most aldehydes occurs at *m/z* 29. What cation does this peak represent? (This fragment is not ethyl cation, $CH_3CH_2^+$, if you don't remember the functional group in aldehydes, check your list of functional groups for help).



21. Which of the following structures is consistent with the mass spectrum shown below?





With the odd molecular mass and a signal at M+1, the compound must be an amine (compound D)

23. An unknown, foul-smelling hydrocarbon gives the mass spectrum and infrared spectrum shown.

a) Use the mass spectrum to propose a molecular formula. How many elements of unsaturation are there?

Molecular mass is 110. Since the compound is and hydrocarbon, it can only be an alkane, an alkene and alkyne
If the compound is an alkane, the standard formula will be $CH_3(CH_2)_nCH_3$
M = 110 = 30 + 14n meaning n = 110 – 30 = 80 = 14n meaning n = 80/14 = 5.71, n most be a natural number. So, the compound is not an alkane.

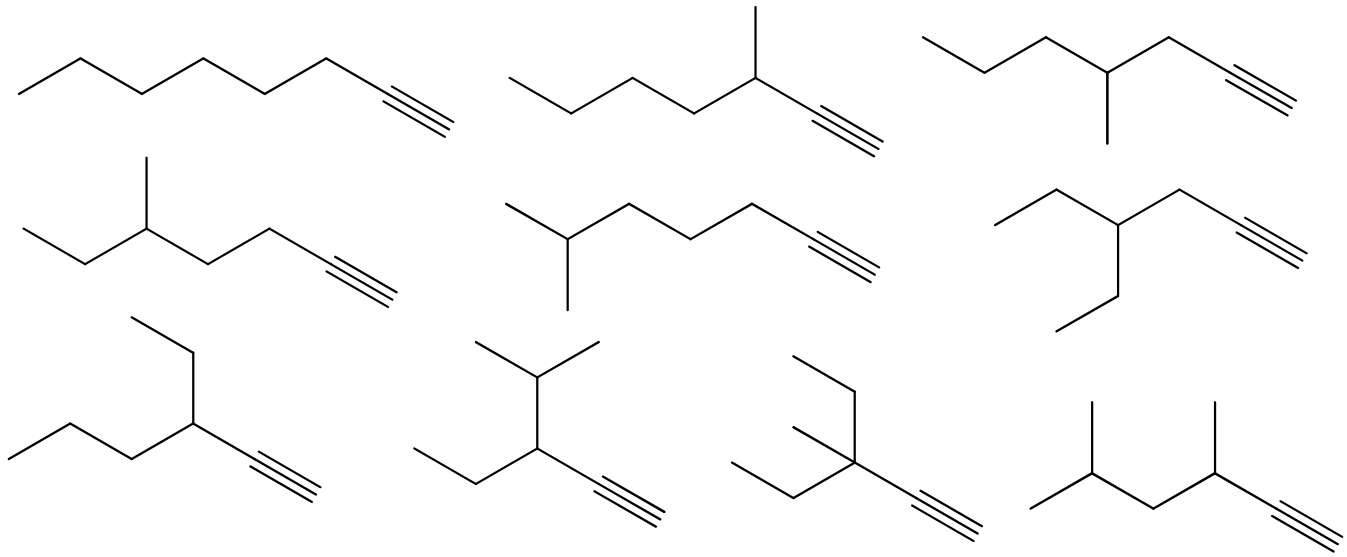
If the compound is an alkene, the standard formula will be $CH_3(CH_2)_nCH=CH_2$
M = 110 = 42 + 14n meaning n = 110 – 42 = 68 = 14n, meaning n = 68/14 = 4.86, n most be a natural number. So, the compound is not an alkene, either.

If the compound is an alkyne, the standard formula will be $CH_3(CH_2)_nCCH$
M = 110 = 40 + 14n meaning n = 110 – 40 = 70 = 14n, meaning n = 70/14 = 5, since n most be a natural number, it is alkyne with 8 carbons: $CH_3(CH_2)_5CCH$.

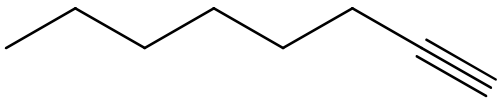
b) Use the IR spectrum to determine the functional group(s), if any.

Since the IR spectrum show the signal for CHsp at 3300 cm^{-1} and the CC triple bond at 2150 cm^{-1}, the triple bond most be terminal.

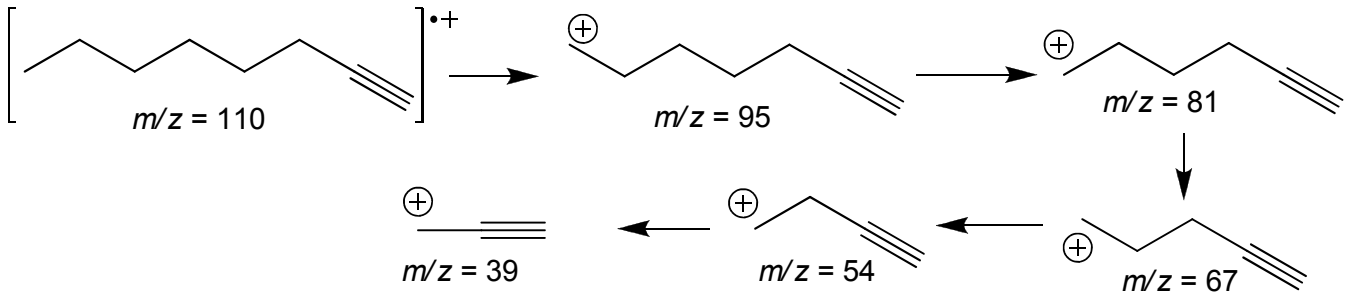
c) Propose one or more structures for this compound. What parts of the structure are uncertain?

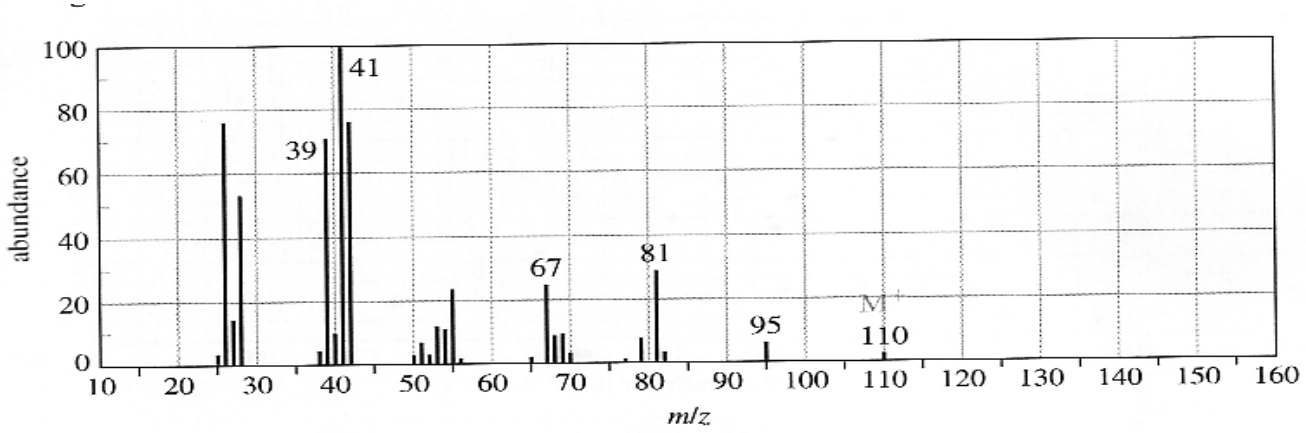


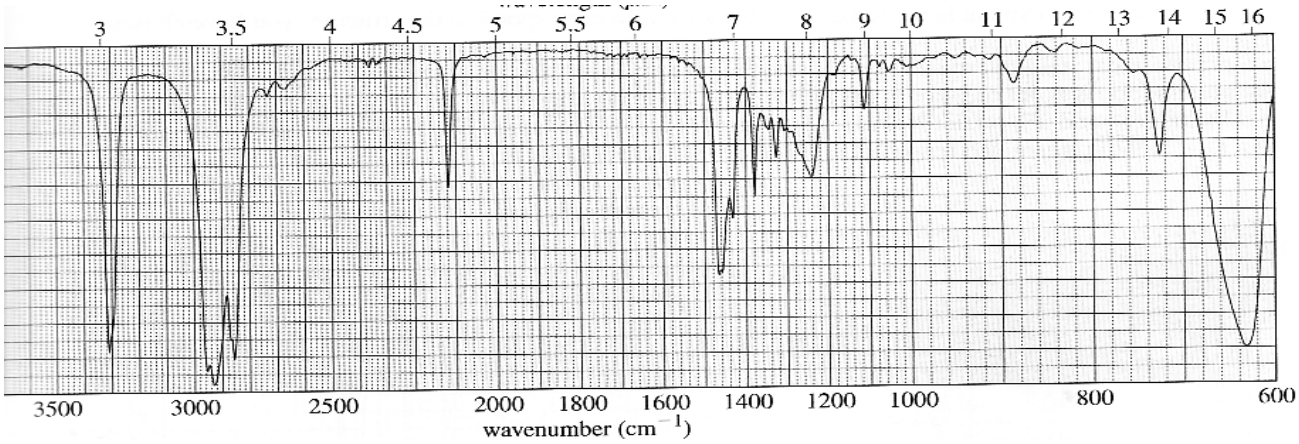
If you knew that hydrogenation of the compound gives n-octane, would the structure still be uncertain?



d) Propose structures for the major fragments at 39, 67, 81 and 95 in the mass spectrum. Explain why the base peak is so strong.




100
80
60
40
20
0
abundance
41
39
67
81
95
M+
110
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
m/z


3 3.5 4 4.5 5 5.5 6 7 8 9 10 11 12 13 14 15 16
3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600
wavenumber (cm⁻¹)