Application of Spectroscopic Methods in Molecular Structure Determination

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Lecture - 19
Mass Spectrometry

Hello, we have come to module 19 of the course on application of spectroscopic methods in molecular structure determination. We are continuing with mass spectrometry and we will discuss more of fragmentation patterns of various types of molecule in this particular module.

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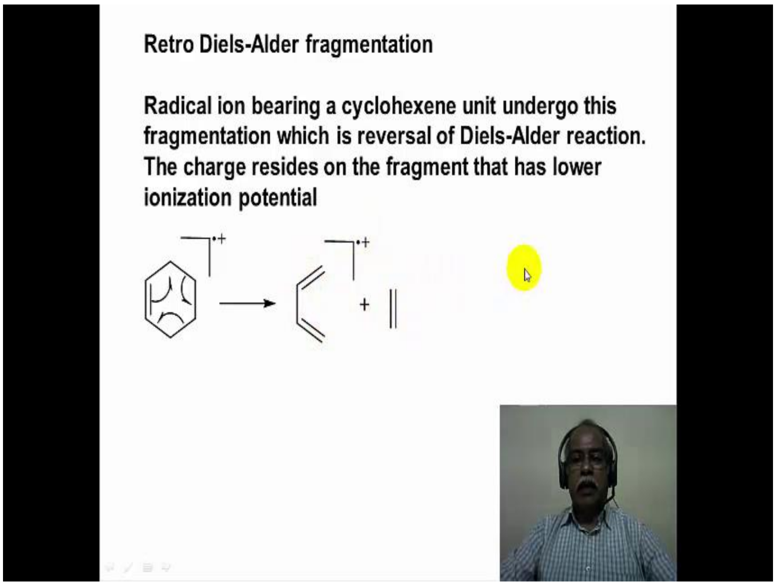

Retro Diels-Alder fragmentation

Radical ion bearing a cyclohexene unit undergo this fragmentation which is reversal of Diels-Alder reaction. The charge resides on the fragment that has lower ionization potential

Now, let us first consider the Retro-Diels-Alder fragmentation. The radical cation bearing cyclohexene unit will undergo this fragmentation which is a reversal of the Diels-Alder reaction. In fact, the Diels-Alder reaction is a 4 plus 2 cyclo addition reactions; what happens here is the reversion of the 4 plus 2 cyclo addition reaction. The charge usually resides in the fragment with the lower ionization potential. If you consider butadiene and ethylene, butadiene will have a lower ionization potential that is why the charge resides with a butadiene which is more stable cation radical than ethylene cation radical.

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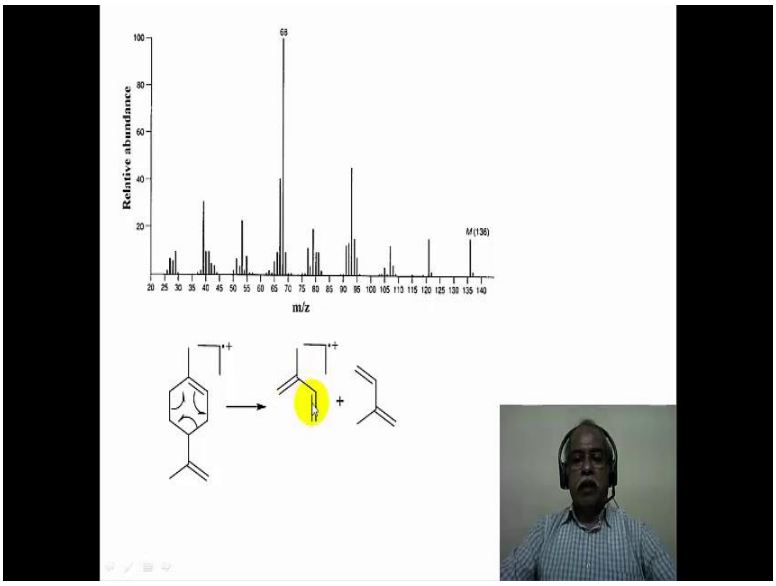

Now, if you can consider limonene, limonene has a cyclohexane ring. It undergoes a Retro-Diels-Alder reaction to produce identical fragment. In fact, limonene is a dimer of two molecules of isoprene and you produce a molecule of isoprene cation radical and a neutral molecule of isoprene. It is only the cation radical that is going to be registered. The molecular rate of limonene is 136, so you see the molecular ion peak here. And you see exactly half of the molecular ion peak at 68. 68 correspond to the isoprene unit and that is the base peak of this particular spectrum. The molecular ion peak has only a small relative abundance of only about 20 percent or so; whereas the fragmented ion is much more abundant in this particular case. So, this is a very classical text book example of a Retro-Diels-Alder reaction of limonene taking place to give isoprene as the fragmented molecule.

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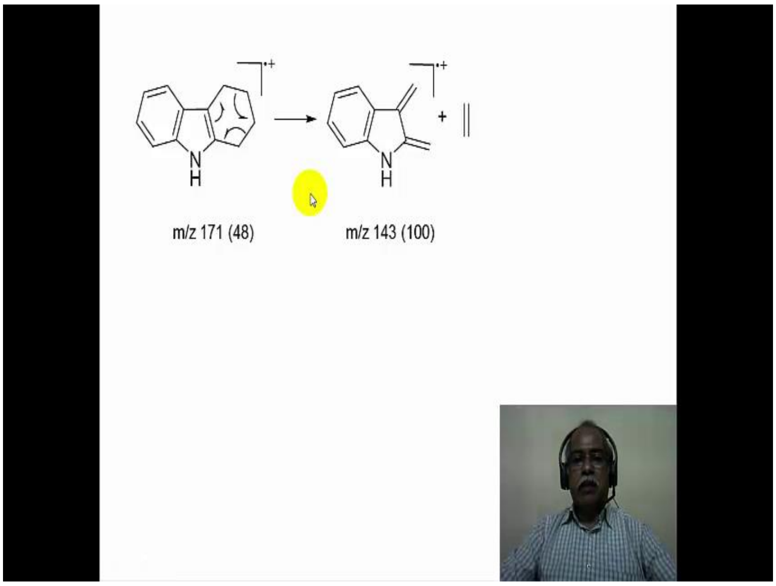

This is tetra hydro carbazol molecule; this has a molecular weight of 171 because it has an odd number of nitrogen. If the molecular weight is also odd, the molecular ion is registered at 171 at 48 percent intensity relative abundance is where there is registered. If we look at this particular ring this a cyclohexene ring, so it undergoes Retro-Diels-Alder reaction. In fact, the base peak in this particular compounds electron impact ionization mass spectrum is, this particular peak at 143 with the loss of 28 units of mass corresponding to the ethylene. So, if you add 28 plus 143 you will get 171, it is a simple fragmentation pattern. It is a Retro-Diels-Alder fragmentation pattern is what we are considering here.

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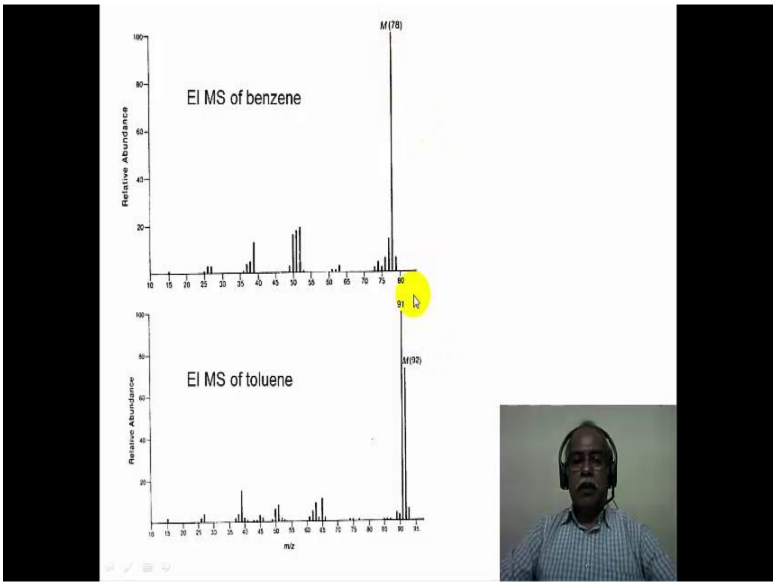

Now, let us consider some electron impact ionization mass spectrum of aromatic compounds. Aromatic compounds as long as they do not have any kind of side chain or a functional group, simple aromatic hydro carbons for example, will register the molecular ion peak as the base peak, benzene is a good example. The fragmentation of benzene molecule is very difficult. So, as a result of this the molecular ion peak itself is the base peak in the case of benzene.

On the other hand, if we take toluene, toluene has CH3 group. So, it can readily lose a hydrogen atom from the CH3 group to produce benzyl cation. In fact, it does so the molecular ion is registered at 92, the benzyl cation is registered at 91, by the loss of one hydrogen from the side chain methyl. So, whenever you have a side chain alkyl substituted benzene derivatives or if you have functional group substituted at benzene derivatives, the molecular ion life time become shorter unlike benzene itself for example, as a result of fragmentation the fragment ions will start showing up in this spectrum.

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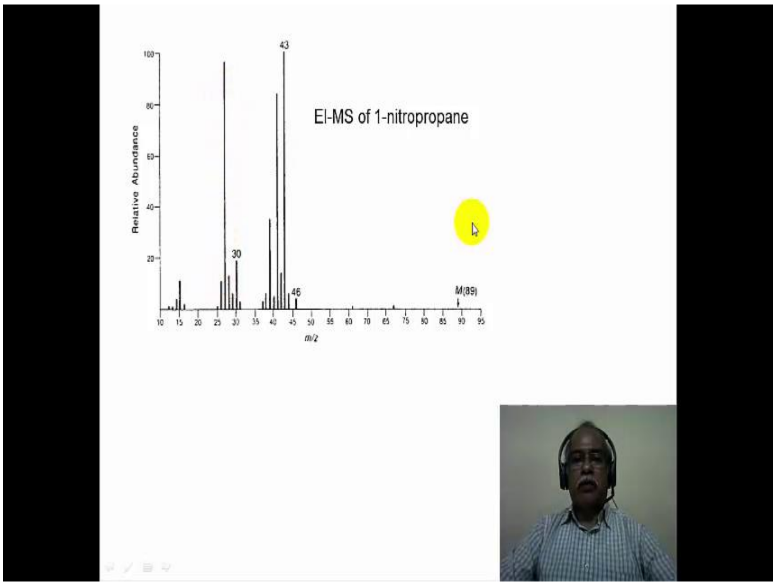
EI-MS of 1-nitropropane

In case of aliphatic nitro compound, loss of 46 mass units corresponds to the NO2 functional group. NO2 functional group corresponds to 46 losses, so 46 losses is essentially corresponding to the loss of a nitro functional group from the molecular ion. In fact, you hardly see the molecular ion intensity at all, just an arrow is showing that the molecular should have come in this position you do not see the molecular ion.

However, loss of 46 corresponds to 43, 43 corresponds to the propyl cation from, in other words NO2 is lost from one nitro propane. So, you get a propyl cation which corresponds to this particular aspect and the propyl cation further can undergo fragmentation pattern to give an ethylene unit and registered at 27 is the ethyl group by the loss of CH3 group in the propyl cation which corresponds to this particular fragmentation pattern.

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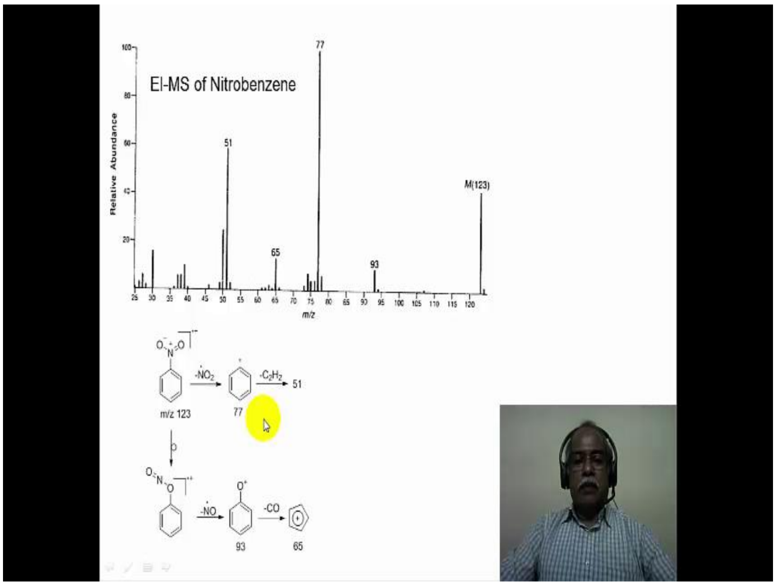
EI-MS of Nitrobenzene

On the other hand, if you look at aromatic nitro compound they do undergo fragmentation, but the molecular ion is registered fairly intense compared to the aliphatic nitro compound, where the molecular ion is not registered at all. So, 123 correspond to the molecular ion peak of the nitro benzene. Nitro benzene can undergo rearrangement to give the phenoxy nitrite kind of a thing. This is a simple rearrangement of nitrogen to oxygen rearrangement is what is happening here. Once it rearranges in this fashion, it can lose NO, which is a radical and it can produce the phenoxy cation. The phenoxy cation can undergo loss of a carbon monoxide molecule to give a cyclopentyl cation, which is registered at 63, 65 and 93 is the phenoxy cation.

So, you see the 93 peak here and the 65 peak also corresponding to this fragmentation. The major fragmentation of course, is a loss of the nitro functional group resulting in the phenyl cation which is at 77 which is the base peak. From the phenyl cation, you lose a molecule of acetylene to give 51 and this corresponds to the peak that is registered at 51 here. So, the spectrum of nitro benzene can nicely interpreted using a mechanism which is shown in this particular scheme of things at the bottom of the spectrum.

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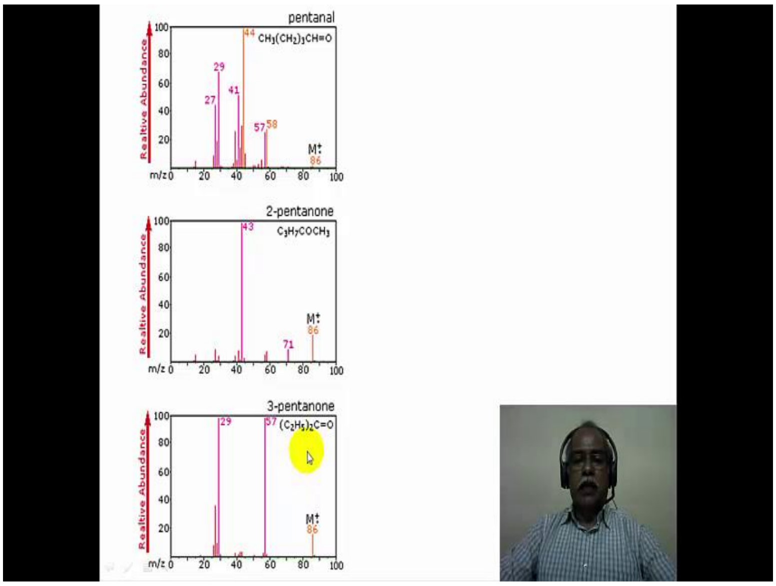

These are some simple organic molecule spectral pattern. The peaks are color coded if you look at the peaks the even molecular weight peaks are given in orange color; whereas the odd molecular peaks are given in magenta color. This is essentially to distinguish even and odd molecular ion peaks that are shown, not molecular ion the fragment ion peaks that are shown in this spectrum.

If you take one pentanal, the molecular weight is 86 and if you lose 28 mass units you will get 58. In other words, it has to lose the molecular ethylene probably undergoes a Mclafferty rearrangement because the gamma hydrogen is available. The gamma hydrogen loss essentially leads to the fragmentation which is the loss of ethylene for example, resulting in the formation of 56. It can also form another fragmentation, this is valeraldehyde, we have seen this spectrum already. This is gamma hydrogen as well as delta hydrogen can be lost in this particular case resulting in the formation of a propane unit corresponding to the 44 mass unit if this particular spectrum and the loss of ethyl group and the loss of with the propyl group and so on essentially gives the fragments which are at 29 and so on.

On the other hand, if you take two pentanone this is a terminal as aldehyde, whereas if you take the internal ketone there is a loss of 15 mass units corresponding to the loss of a methyl group. This is 15 mass unit differences 86 minus 15 is 71 and then the loss of propyl group which produces an acetyle cation, it can also produce a propyl cation, but acetyle cation will be resonance stabilized. So, that comes as the base peak at 43. In fact, three pentanone again has a simple fragmentation pattern loss of 29 mass units corresponds to 57. So, essentially register 29 which is ethyl cation and 57 which is due to the propyl propanol cation that is C2 H5 CO plus is what is registered at 57 in this spectrum. Spectrum is fairly simple where a molecule is a symmetrical molecule here.

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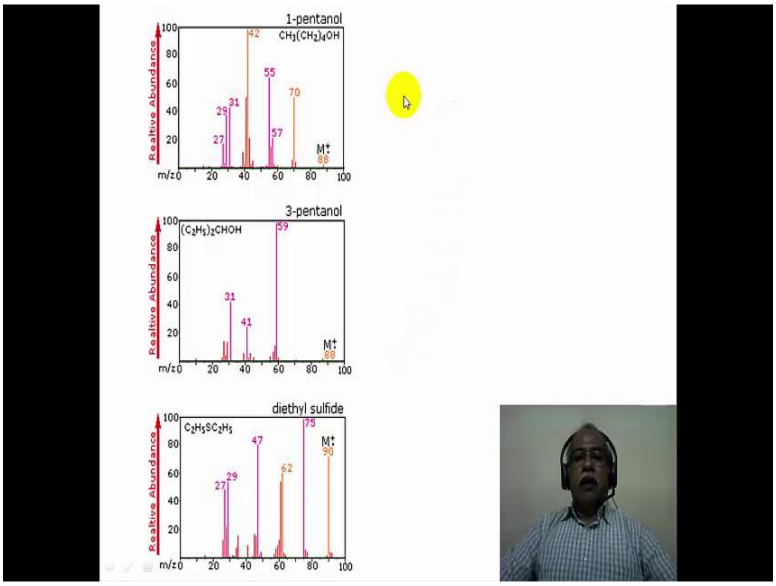

In the case of alcohols, the most prominent peak generally seen is the loss of water, mass unit of 18 is lost the molecular weight is 88, 88 for one pentanol, if you lose some molecule of water you get the corresponding 70 molecular weight and from 70 molecular weight if it undergoes a Mclafferty rearrangement it will produce an alkene that can undergo Mclafferty rearrangement loss of 28 mass units will produce 42. The other mass units are simple alkyl losses are what is seen here as the odd molecular ion peaks in this particular system. In the case of pentanol the 59 peak is the registered as the base peak in this particular case, this is essentially loss of 29 mass units is what is lost in this particular case.

In the case of diethyl sulfide for example, there is a loss of a methyl group which corresponds to the fragment corresponding to 75 for example, and the other molecular weights are also seen because of the subsequent fragmentation of the ethyle sulfide the 29, 27 are coming from the ethyle group for example, and the 47 could be coming from the loss of a methyl group which results in the formation of a CH2 double bond S plus CH2 CH3 that kind of a group will come around 75 or so with the loss of methyl group.

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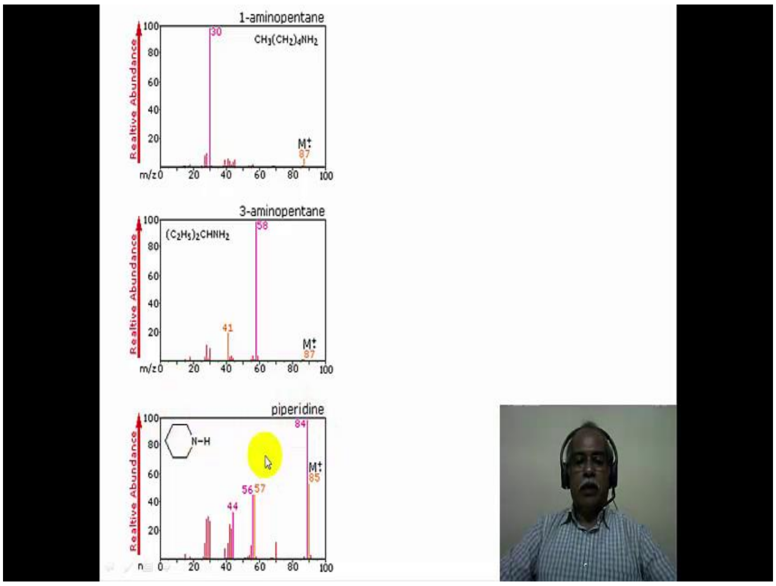

In the case of amine, the most fundamental fragmentation essentially the amine cation radical essentially loses an alkyl chain in the b alpha beta position. So, this will result in CH2 double bond NH2 plus iminium cation what is formed. The iminium cation is registering at 30 mass units and the parent molecular ion is registering at 87. So, it loses this C3 fragment in this particular case, this is C5 fragment. So, C4 will be lost CH2 double bond NH2 is seen as the peak corresponding to the 30 mass units. In the case of three aminopentane this is essentially a fragmentation resulting in the formation of an even electron species. So, it is a simple fragmentation is what is taking place. So, one can figure out the alkyl group that is responsible for this simple fragmentation this would be 29.

So, the ethyle group is essentially lost in this particular case to produce a fragment of corresponding to molecular weight of 58. In the case of cyclo cyclic amines for example, fragmentation is minimized, we can see here the amine cation radicals are hardly seen in this two spectra where as in this cyclic amine spectrum because we need to fragment two bonds it does not undergo fragmentation. So, readily except for the loss of the NH hydrogen which is registered at 84 otherwise the molecular ion has a fairly intense peak at 60 percent relative abundance base peak is a loss of hydrogen atom from the molecular ion to produce the corresponding iminium ion in this particular case.

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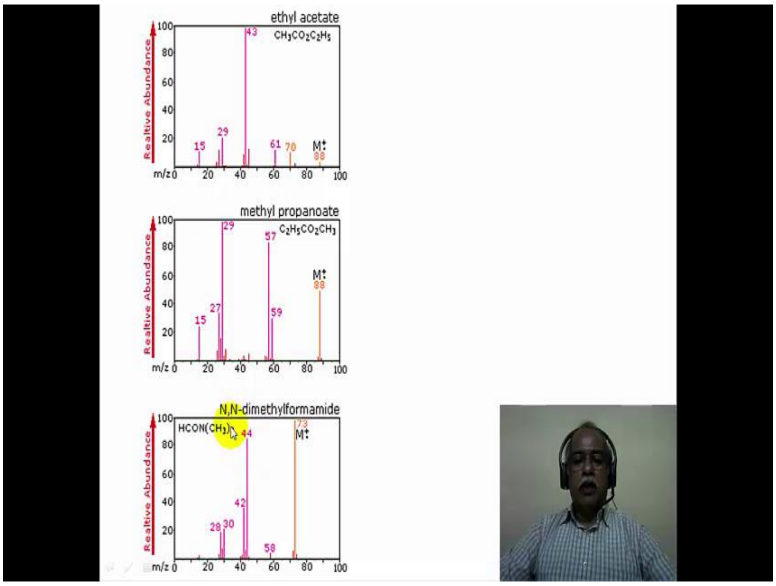

These are again molecules which are fairly simple ethyl acetate for example gives a peak at 43 because of CH3CO with loss of C2H5O in this particular case. In other words, an ethoxy group is lost and the acetyle group is registered at 43 peaks at 43 mass units for example. This is methyl propanoate; methyl propanoate can essentially undergo fragmentation to give 57 and 29 by the loss of methyl group and loss of the ethoxy group essentially 31 loss is what is going to give this particular peak.

57 is coming from the loss of the methoxy peaks for example, and the loss of ethyle peak is what is going to give the 29 fragment in this particular case. NN dimethylformamide has a molecular weight of 73 from that 73 a simple fragmentation produces 49 for example, which could be loss of one of the methyl groups or the NN dimethyl group for example, corresponding to the particular difference between these two is about 29 or so,

that could be loss of the formyl group also resulting in the formation of NN dimethyl cation radical which corresponds to the 44 mass unit.

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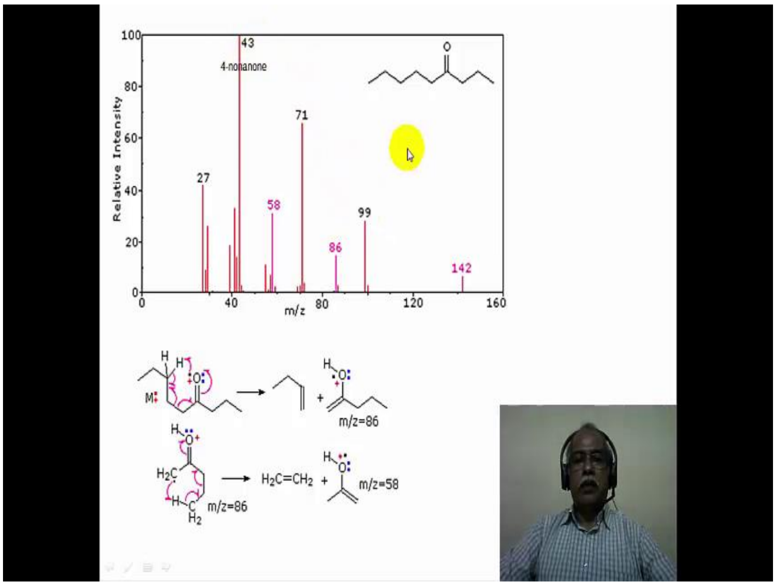

This is a four Nonanone, this is a linear ketone, this under goes the Mclafferty rearrangement quite readily to give this particular fragment at 86. The Mclafferty rearrangement essentially loss of the alpha fragmentation results in the formation of this particular fragment which is at 86. So, you see 86 fragments and the 58 fragment as a prominent fragment in this case which is the neutral molecule elimination from the 142 and in subsequent simple fragmentation produces all this odd electron odd number mass number units are produced by simple fragmentation.

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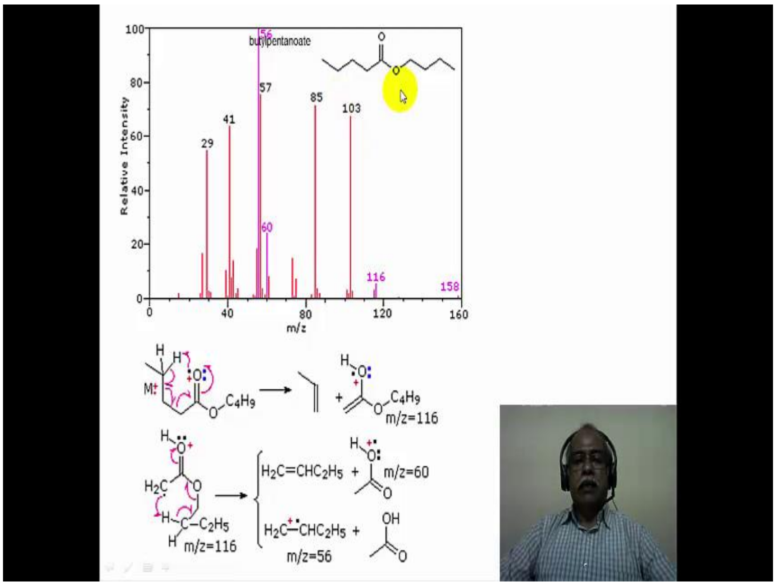

This is butyl pentanoate this is an ester again capable of undergoing Mclafferty rearrangement the mechanism is shown here very clearly and the various fragments that are formed corresponds to the various fragments that are produce correspond to the magenta colored items, which are the simple loss of ethylene or propane in this particular case for example, through the Mclafferty rearrangement.

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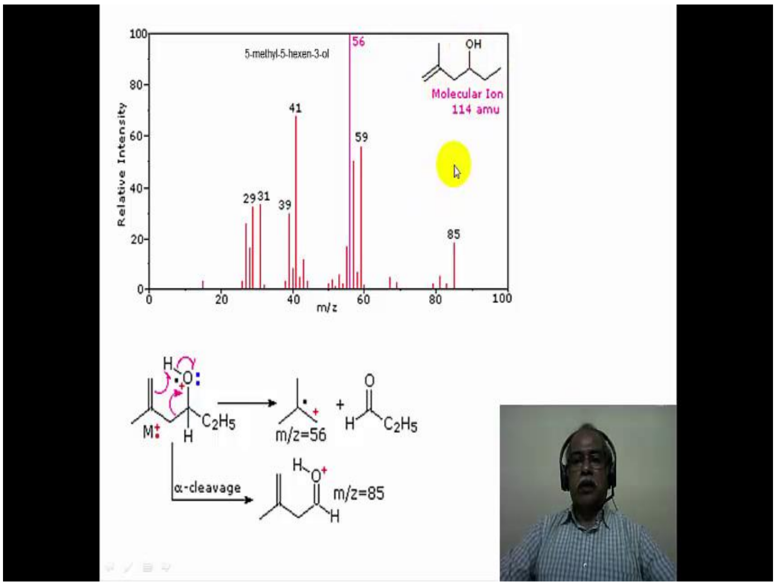

Again, another kind of Mclafferty rearrangement, the molecular ion itself is not seen, but the Mclafferty rearranged product is which is this particular cation tertiary butyl kind of a cation is registered at 56 in this spectrum of the alcohol that is shown the structure of which is shown here.

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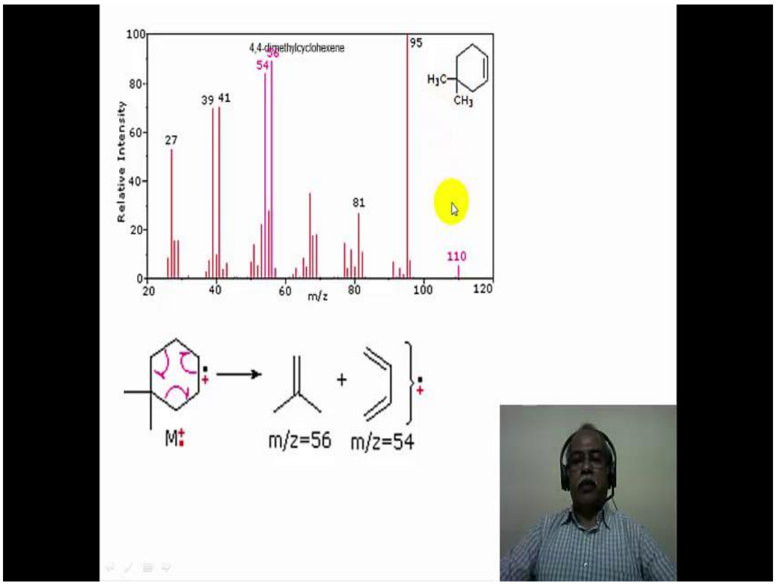

This is a simple cyclohexene unit. So, it can undergo of fragmentation pattern. Now, you have a dimethyl substituted ethylene and a butadiene probably their ionization potentials are nearly the same. The fragments are registered at 56 and 54 they are both equally intense in this particular case for example, and a loss of a methyl group from the molecule will essentially result in the formation of 95 from 110. If you subtract 15 from this, you get 95 which is loss of a methyl group from this particular molecule.

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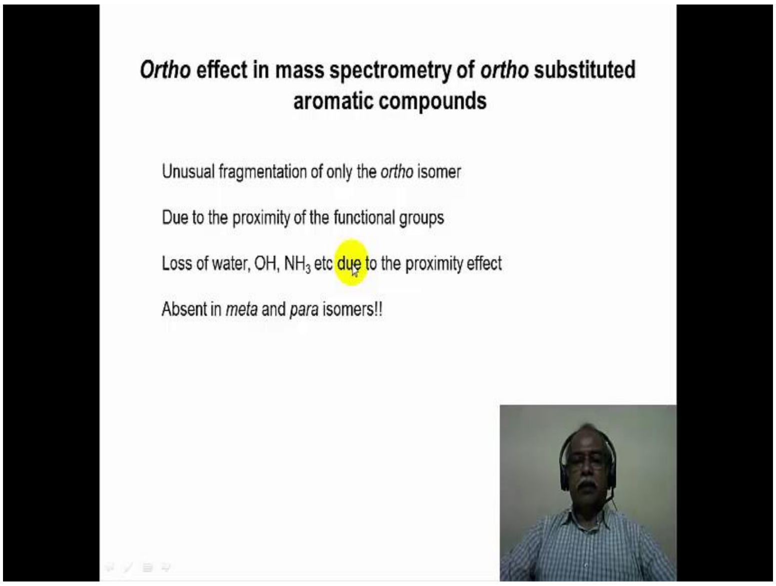

Ortho effect in mass spectrometry of *ortho* substituted aromatic compounds

Unusual fragmentation of only the *ortho* isomer

Due to the proximity of the functional groups

Loss of water, OH, NH_3 etc due to the proximity effect

Absent in *meta* and *para* isomers!!

Now, let us consider a special effect called ortho effect. In the mass spectrometry of ortho substituted aromatic compound, ortho substituted aromatic compound show a particular unusual fragmentation only characteristic of the ortho isomer. It is not present in the meta isomer or the para isomer, this is essentially due to the spatial proximity of two functional group that are present in the ortho isomer, what is normally seen is a loss of simple molecules like water, OH and NH3, etcetera are the once that are producing the proximity effect because of the ortho substitution.

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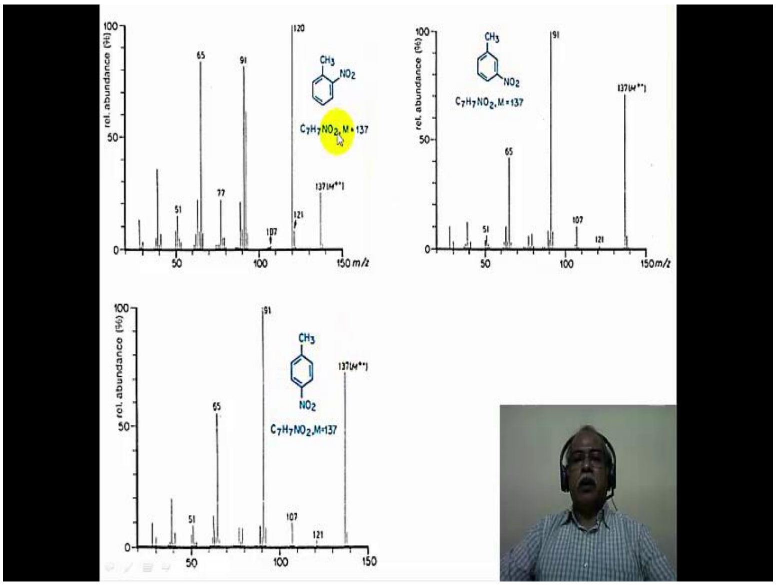

This is illustrated in the example of ortho nitro toluene, meta nitro toluene and para nitro toluene. Ortho nitro toluene loses a molecule of water, the molecular ion is 137 for example, it loses 17 mass unit which is OH loss for example, the OH loss essentially comes because of the oxygen and the methyl hydrogen are in close proximity in the Ortho substituted derivative. So, that loss is registered at 120 and this is a base peak corresponding to a structure where you will have CH2 double bond N double bond O kind of a structure. In other words, an ortho quinonoid structure kind of a thing you can write for the 120 fragment. You can see here distinctly the other isomers lack that particular peak at 120 and essentially this peak is coming from the molecular ion undergoing a loss of OH peak OH 17 mass unit corresponding to 120 which is very characteristic feature of only the ortho isomer and not the meta and para isomer. The other fragments are fairly simple fragment 91 is essentially produced by loss of HNO2 in this molecule resulting in the formation of a benzene cation kind of a system and this is registered in all the three isomers. From the 91 one can get 65 by the loss of unit of acetlyene is the lost for example and that will produce 65 these are typical fragmentation pattern the 91, 65 and so on are typical fragmentation pattern of a benzenite kind of a compound.

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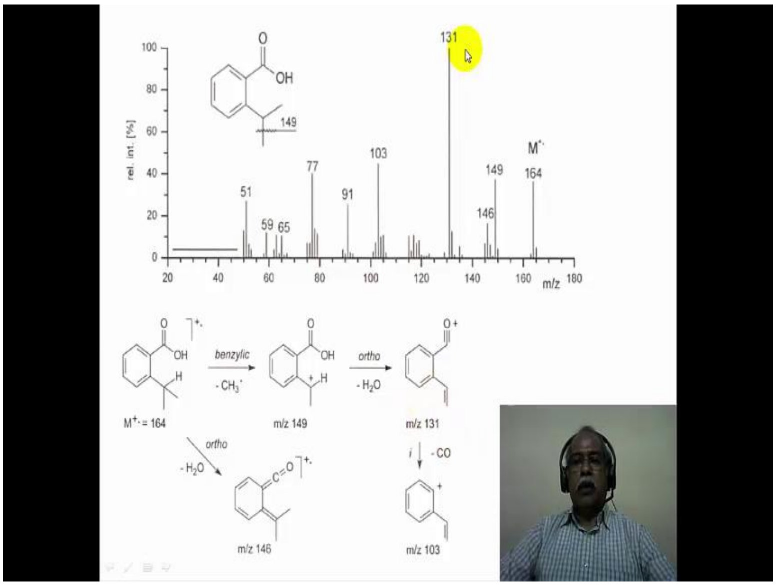

Here is another example of ortho effect; this is an ortho isopropyl benzoic acid this loses a molecule of water during the ortho effect process producing ion at 131 which is registered as the base peak. So, this is just additional example of an ortho effect kind of a thing here.

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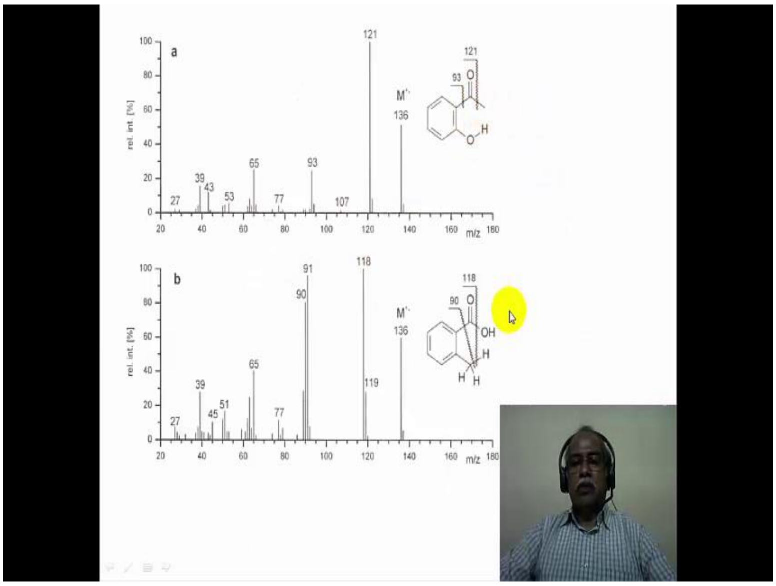

Some more example, ortho hydroxyacetophenone and ortho toluic acid for example, they also produce by loss of water. In this two cases production loss of water corresponds to the peak at 118 which is base peak in this particular case from 136 molecules minus 18 is lost here.

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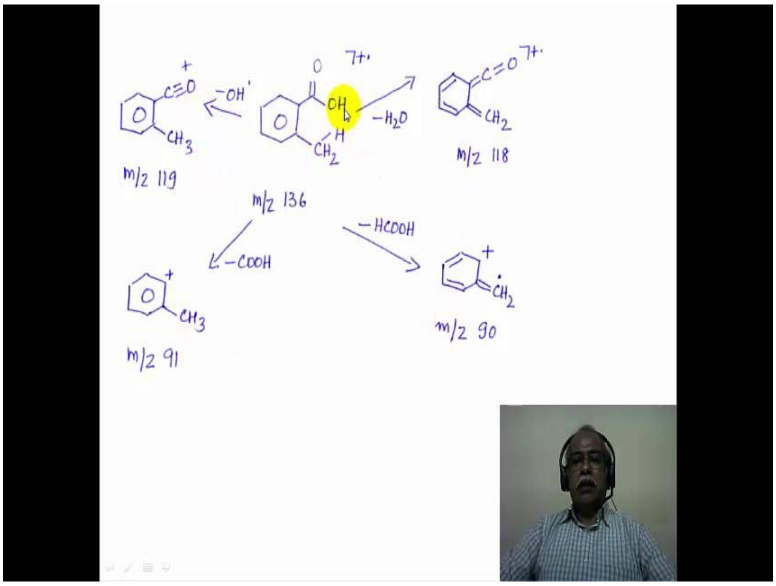

The mechanistic scheme is shown here for the loss of water and the loss of other fragments resulting in the formation of various ion corresponding to the ortho toluic acid the spectrum of which is shown in this particular slide.

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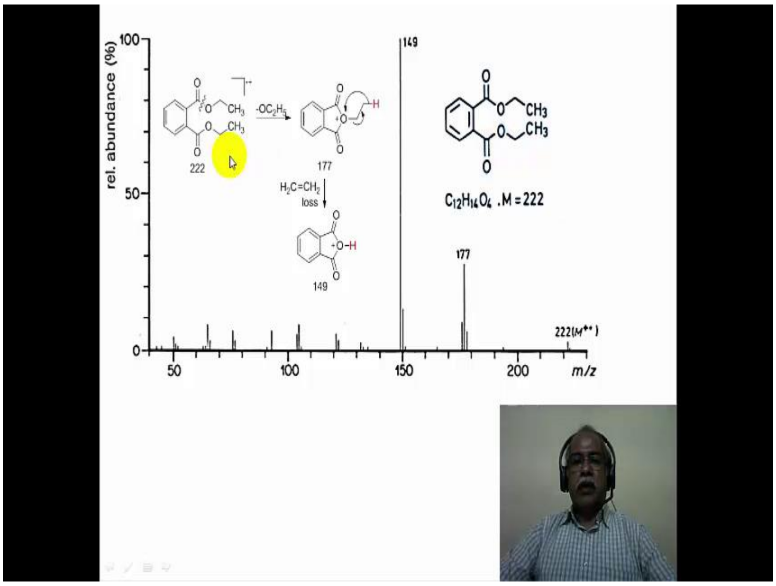

This is diethyl phthalate; diethyl phthalate also undergoes an ortho effect. Initially, the bond cleavage alpha fragmentation results in the formation of an alkylated phthalic anhydride kind of a structure. The molecular weight of the compound is 222 loss of an ethoxy group puts the fragmented molecule at 177 further loss of ethylene because this is an oxonium ion kind of a rearrangement, beta hydrogen is transferred on to the oxygen and a molecular ethylene is lost. So, 177 minus 28 essentially correspond to 149 and that is registered at the base peak. This is very characteristic of again the ortho isomer of the phthalic acid kind of system is what responds to this kind of a rearrangement process.

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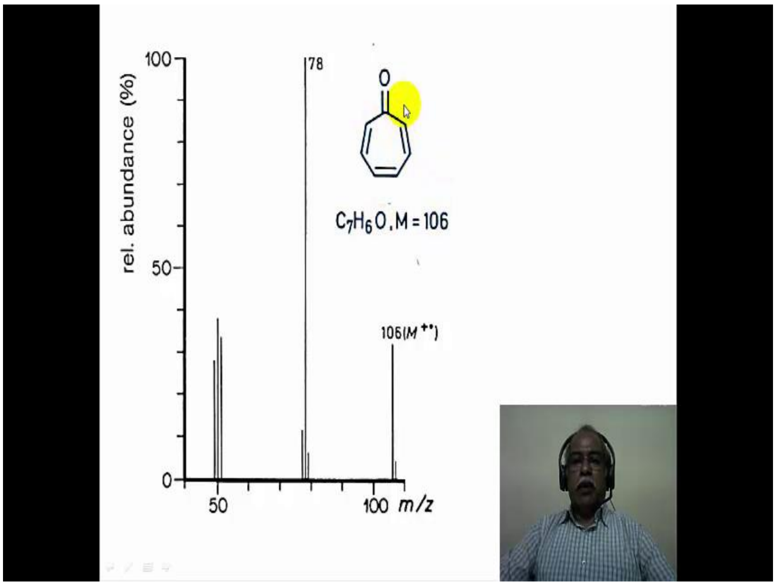

This is Tropone. Tropone can eliminate the molecule of carbon monoxide conveniently from the molecular ion to setting the formation of 78 which is benzene cation radical. From the benzene cation radical, you can decompose to get this fragments by loss of acetylene units from the benzene unit.

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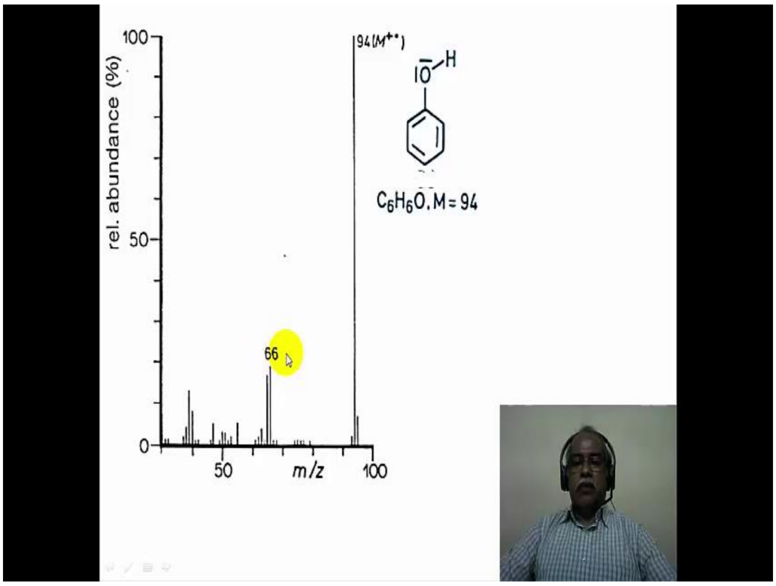

Phenol also undergoes a very similar fragmentation; the keto form of phenol can undergo carbon monoxide elimination. So, essentially loss of 28 is what is seen to register the 66 and the 28 loss is because of the carbon monoxide elimination from the keto form of the phenol. In other words, in the gas phase there should be sufficient concentration on the keto form of phenol which undergoes the elimination of 28 mass unit which corresponds to carbon monoxide.

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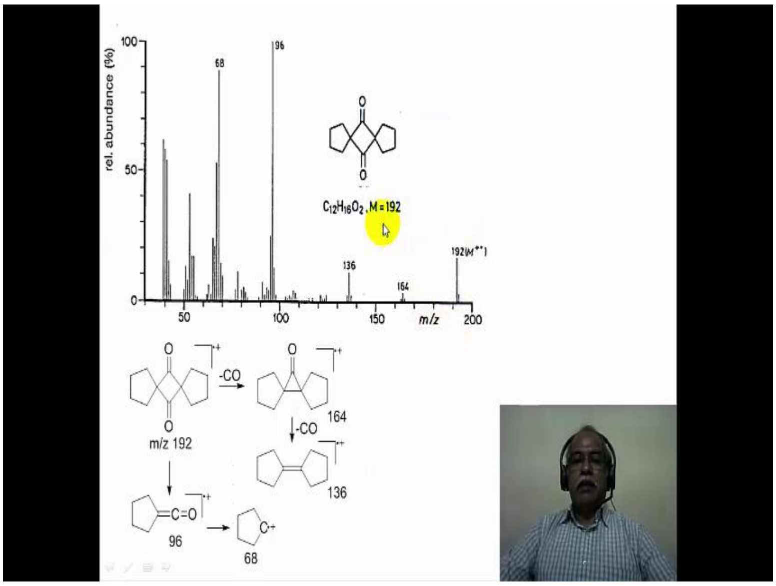

Here is a spyro keton is a very interesting fragmentation that is taking place the molecular weight is 192, a symmetrical fragmentation of these two bonds produces this ketene kind of a system which has a molecular weight of about 96 and that is registered as the base peak in this particular spectrum. It can also lose carbon monoxide in a sequential manner as it is shown, first loss of carbon monoxide puts a ion at 164. Subsequent loss of carbon monoxide put another ion at 136 for example; loss of carbon monoxide from in this ketene unit produces this cyclic carbenium ion which is at 68 which is also a very intense peak in the molecule spectrum of this particular spyro like keton.

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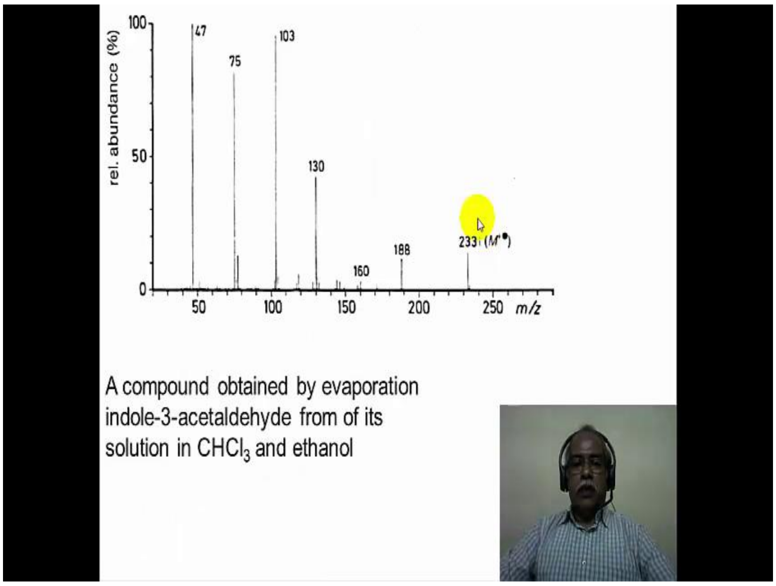

A compound obtained by evaporation indole-3-acetaldehyde from of its solution in $CHCl_3$ and ethanol

Now, I leave you with two puzzles, you can solve this puzzle. We will consider the solution for these puzzles in the next class. If you consider indole, indole is a hetro cyclic system where it is benzene fused to aperol system is called indole 3 acetaldehyde is what is given, indol 3 acetaldehyde is evaporated from solution of chloroform at ethanol some reaction is taking place aldehydes typically react with ethyl alcohol. So, think of a reaction between all aldehyde and ethyl alchohol and that particular compound that is resulting from this aldehyde is registered with a molecular weight of 233 and these are the fragment ions that are produced. So, identify the molecule that is responsible for the mass spectrum that is shown here.

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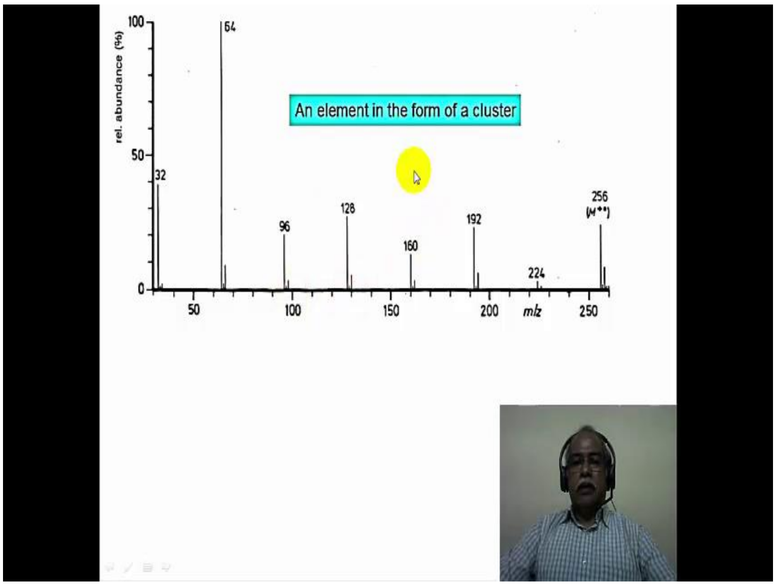

An element in the form of a cluster

It is not indole 3 acetaldehyde mass spectrums; it is a product that is obtained by evaporating indole 3 acetaldehyde from ethyl alcohol and chloroform. It is a ethyl alcohol that is going to react with the aldehyde. Think of a problem like that and see we can solve this structure. Here is a simple question; an element in the form of a cluster gives this molecule in this mass spectrum that is shown here. If you look at the subsequent loses each loss is a 32 mass unit. So, you have to think of an element with 38 two mass unit resulting in the fragmentation like this, think about it is a fairly simple problem. We will address this problem in the next module also. So, in this particular module what we have considered so far is the fragmentation of many different types of organic compounds and we consider the fragmentation including the Retro-Diels-Alder fragmentation and this kind of a fragmentation interpretation is what makes the mass spectrometry technique a very valuable tool in terms of the structural elucidation of organic compound.

Thank you for your attention.