

The Mass Spectra Analysis for α -Ionone and β -Ionone

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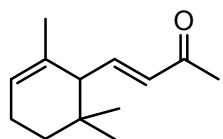
Abstract

The presented work of this paper will be the first of a series of MS spectral analysis for some selected well-known compounds. In here the target molecules to have their MS spectra analyzed are α -Ionone and β -Ionone. The analysis will be in detail and show the mechanism of how the major fragments are formed in the mass spectrophotometer; hence, this paper is for educational purposes that could serve both students and instructors.

Keywords: α -cleavage, β -cleavage, Retro Diels-Alder, base peak, α -Ionone, MS spectrophotometer

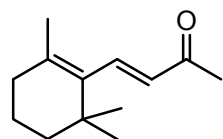
1. Introduction

The Ionones, Damascones, and Damasconones are groups of compounds known as rose ketones. Ionones (α , γ) are aroma compounds found in some essential oils, a volatile oil of the plants from which they were extracted, such as rose oil. α -Ionone, (3*E*)-4-(2,6,6-trimethyl-2-cyclohexenyl)-3-butene-2-one and γ -ionone, (3*E*)-4-(2,2-dimethyl-6-methylenecyclohexyl)-3-butene-2-one, are the main contributors to the aroma of roses and it is an important fragrance used in perfumery (Diez, Maros, Apesteguia, & Cosimo, 2009); whereas, β -Ionone, (3*E*)-4-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2-one, is used in vitamin A synthesis. α -Ionone and β -Ionone combined are considered characteristic of the scent of violets (Leffingwell, 2005., Aiyeloagle, & Ekundayu, (2005).



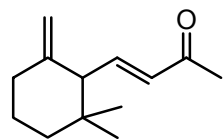
α -Ionone:

(3*E*)-4-(2,6,6-trimethyl-2-cyclohexenyl)-3-butene-2-one



β -Ionone:

3*E*)-4-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2-one



γ -Ionone:

3*E*)-4-(2,2-dimethyl-6-methylenecyclohexyl)-3-butene-2-one

Mass spectrometry is not a form of spectroscopy in the conventional sense, because no radiation is absorbed or released; however, mass spectrophotometer is considered by many chemists as the second most useful machine regarding structural elucidation of organic compounds. It is a high sensitive technique (I ng) of sample and contrary to the spectrophotometric techniques it is a destructive method.

A sample being studied will be vaporized once injected into the machine, then ionized, analyzed, detected, and recorded as MS spectrum respectfully (Solomons, Fundamentals of Organic Chemistry).

Each one of the five steps mentioned above takes place in the mass spectrometer in its five parts: sample inlet, ion source, mass analyzer, detector, and signal recorder.

The two major sources of ionization methods, converting the vaporized sample to ions, are Electron Ionization (EI) and Chemical Ionization (CI). The mass analyzer separates the ions based on their mass-to-charge ratio (m/z). The first and most used analyzer is called quadruple mass analyzer.

Upon the ions separation, the detector reads and counts them, and then a PC records and process the signals to give the mass spectrum (Vollhardt, & Schore, Organic Chemistry; Pavia, Lampman, Kriz, & Vyvyan, Introduction to Spectroscopy).

2. Spectral Analysis

As shown in Figure 1, the characteristic fragments of α -Ionone are the ones where the numbers are indicated on the signals. These signals represent the mass-to-charge ratio for the fragments. The method used in the ionization for the sample being studied is the EI (Pavia, Lampman, Kriz, & Vyvyan, Introduction to Spectroscopy). Electron-impact-induced ionization of α -ionone involves loss of an electron from the lone pair, an unshared pair of electrons, or from the π bond leads to the formation of molecular ion plus the rest of fragments.

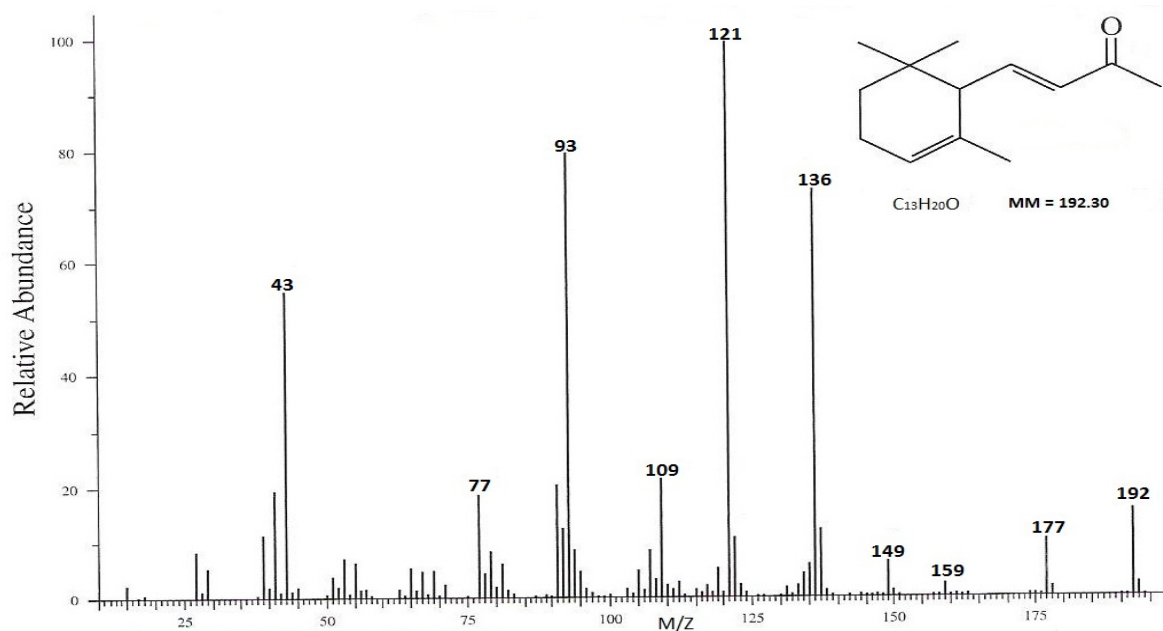
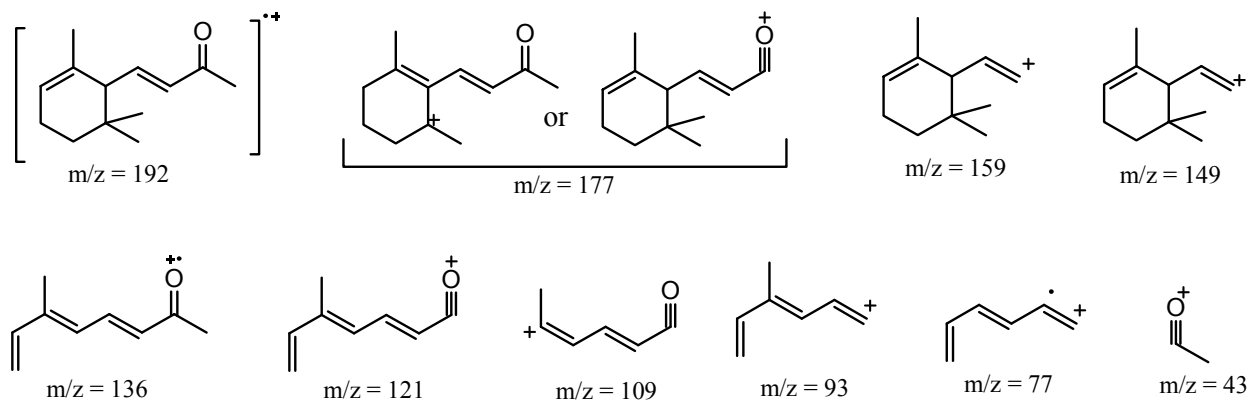


Figure 1. EI-MS of alpha-Ionone

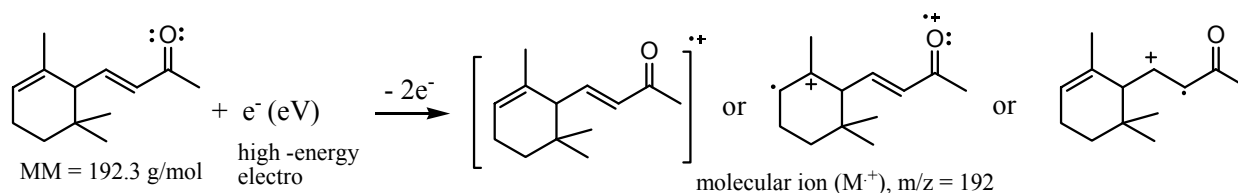
3. The Structures of the Major Fragment Ions



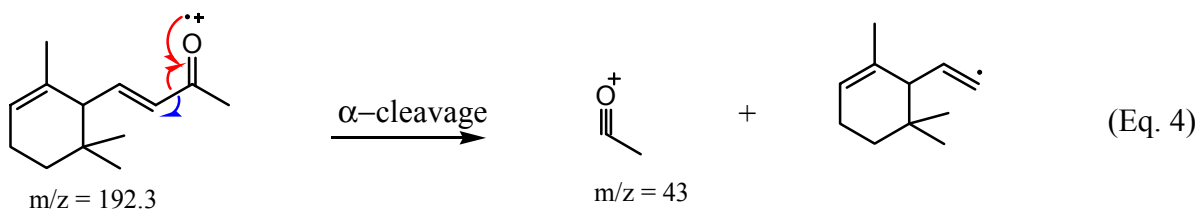
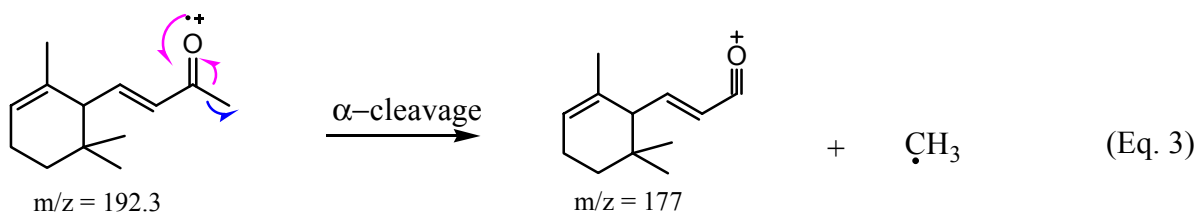
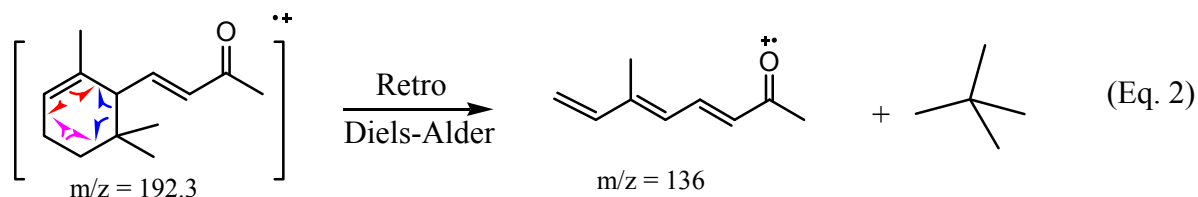
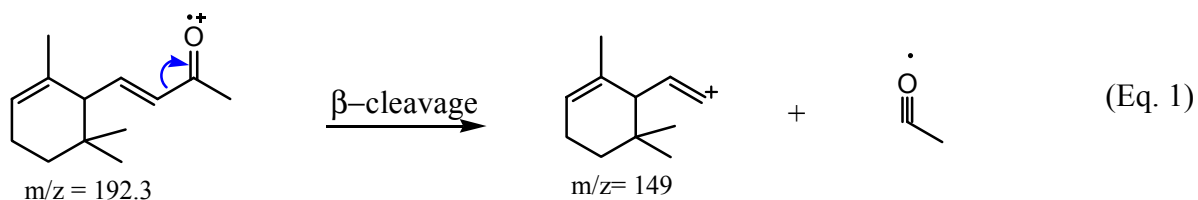
4. Fragmentation Mechanism

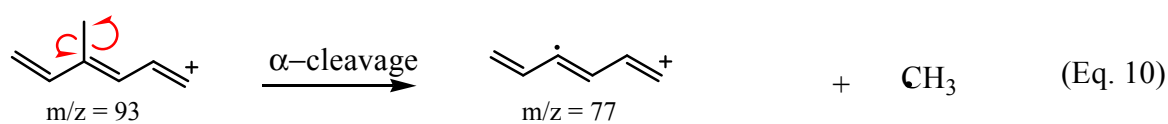
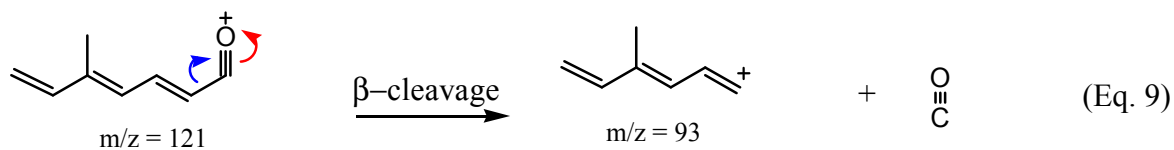
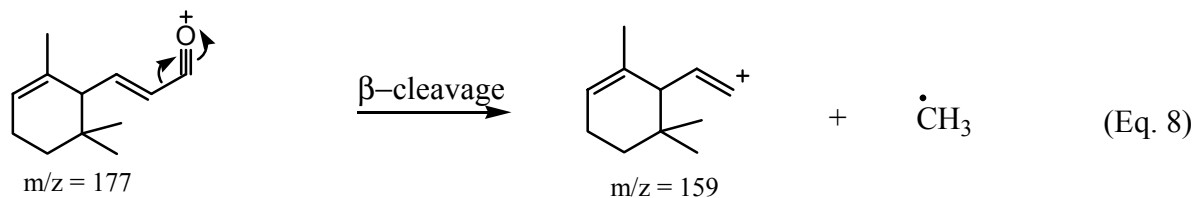
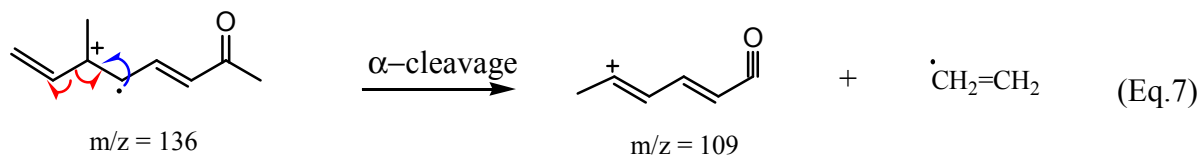
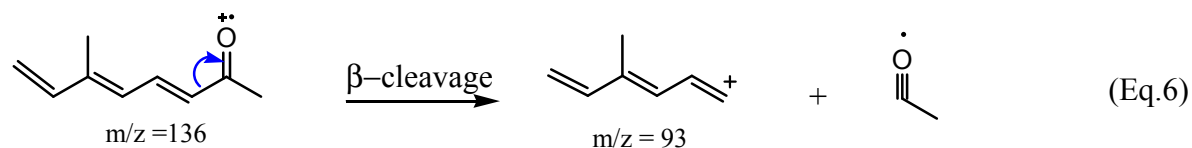
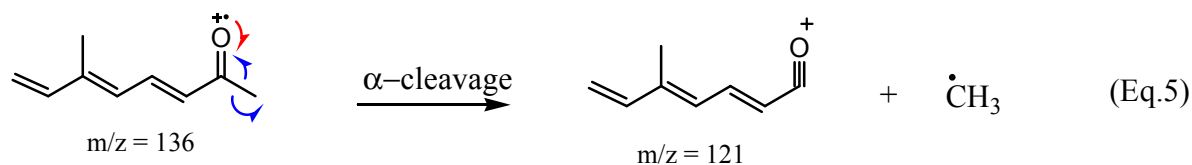
A. α -Ionone Fragmentation:

Once a sample of Ionone is introduced to the machine, it will be vaporized and then bombarded with a beam of high-energetic electrons (usually 70 eV, or about 1600 Kcal/mol) in the ionization chamber, an electron will be knocked off of the molecule leading to the formation of a positively charged ion called the molecular ion, M^+ , as shown below

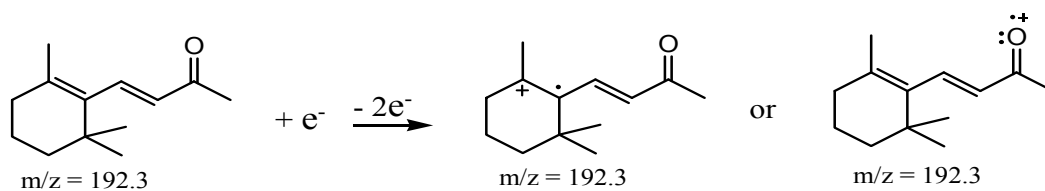


The molecular ions, and due to the high energy imparted in the ionization chamber, may break into smaller pieces (fragments). The Ionone ions may fractionate in various characteristic ways, where one fragment carry the charge and the other one remains uncharged. The following fragments are considered characteristic ones that are formed through α -cleavage, or β -cleavage, or Retro Diels-Alder Rearrangements.





B. β -Ionone Fractionation



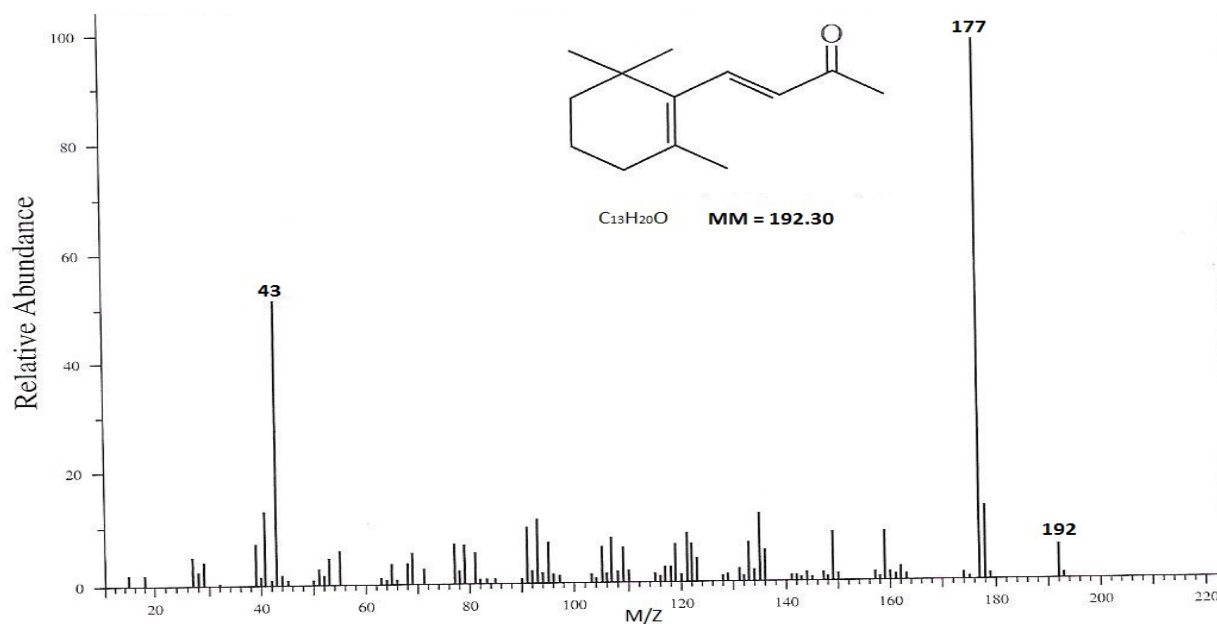
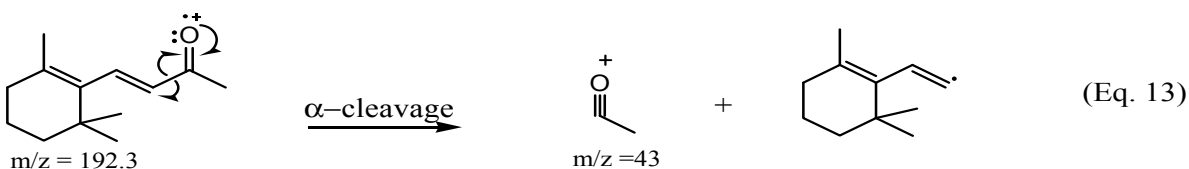
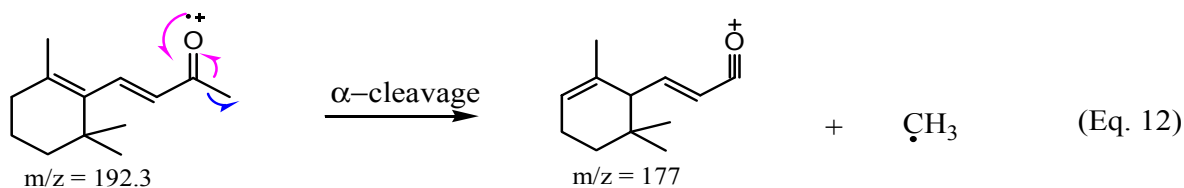
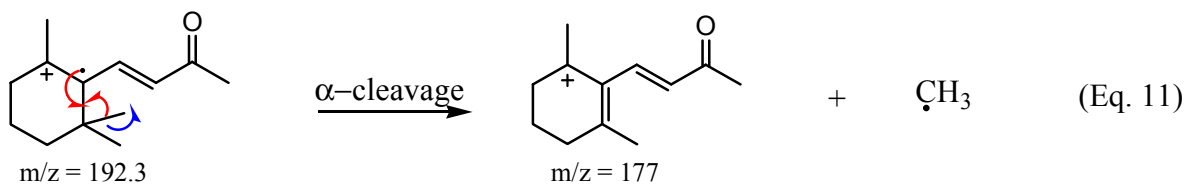


Figure 2. EI-MS of beta-ionone

5. Discussion

Cleavage of molecular bonds in the EI-Mass Spectrometer will lead to charged and neutral fractions. There are well-known five characteristic cleavages that take place, such as, α -cleavage, β -cleavage (known as inductive cleavage), Retro Diels-Alder cleavage, Two-bond cleavage, and McLafferty cleavage (Rearrangement). Some or all of these characteristic fragmentations might take place depending on the compounds being fragmented.

Only the ionized fractions, usually carry one positive charge, can be detected and leads to singlet peaks as a function of their m/z ratio. The peak intensity depends on its number of ions formed; the most abundant ions will give rise to the tallest peak in the mass spectrum, called the base peak. The signal of molecular ion, M^+ , if appears will be the highest m/z ratio of the spectrum not to confuse with $M + 1$ and $M + 2$ isotopic peaks.

Regarding α -Ionone's mass spectrum, the peak of weight $m/z = 192$ is the molecular ion peak and the smaller peak of weight $m/z = 193$ is the isotopic peak of $M + 1$.

The α -Ionone molecular ions undergo two major cleavages to lose the methyl acylium radical due to β -cleavage and 2,2-dimethyl propane due to Retro Diels-Alder cleavages respectively and form two fractions of the positively charged vinylcyclohexyl ion at $m/z = 177$ and 6-methyl-3,5,7-octatrienone ion at 136 respectively. (Eq. 1 & 2)

Furthermore, two α -cleavages of the molecular ion break into a methyl radical and the corresponding positively charged ion of weight $m/z = 177$ as well as the methyl acylium cation at $m/z = 43$ with the corresponding radical vinylcyclohexenyl moiety. (Eq. 3 & 4)

Usually, fragmentations take place not only on the molecular ion, M^+ , level but also on the level of other fragments that might go a second or a third mode of fragmentations. The fragments at $m/z = 136$ undergo α - and β -cleavages to lose a methyl and acylium radicals respectively and form two fragments at $m/z = 121$ (the base peak, the most abundance fragment) and 93 respectively. (Eq. 5 & 6)

Besides the α - and β -cleavages of fragments at $m/z = 136$, it also loses a vinyl radical through α -cleavages to form fragments at $m/z = 109$. (Eq. 7)

The fragments at $m/z = 177$ undergo β -cleavages to lose a methyl radical and to form the vinylcyclohexenium ion at $m/z = 159$. (Eq. 8)

Furthermore, the commonest fragment ion, $m/z = 121$, undergo β -cleavages to lose carbon monoxide and form another characteristic peak of weight $m/z = 93$. (Eq. 9)

Further cleavage of $m/z = 93$ leads to the loss of a methyl radical and the formation of the ionized fraction at $m/z = 77$ fraction. (Eq. 10)

The β -Ionone molecular ions undergo three major α -cleavages to lose methyl radical, methyl radical, and the radical moiety at $m/z = 149$ respectively and form the positively charged fragments at $m/z = 177$ & 177 & 43 respectively. (Eq. 9, 10, & 11)

For β -Ionone spectrum, only two major peaks are present at $m/z = 177$ and 43 comparing to several major ones for α -Ionone. Due to the absence of the fragment ions of weight $m/z = 136$, Retro Diels-Alder Rearrangement is prohibited which contributes to this low of fragmentations, hence, several peaks at $m/z = 77$, 93 , 121 , and 149 are missing or in low abundance. Also, and based on the MS-spectrum of β -Ionone, and since many of the fragmentation processes in mass spectrometry proceeds so as to form a stable carbocation, it indicates that the fraction moiety at $m/z = 177$ is somewhat stable and it is the most abundance, hence, it is considered as the base peak.

6. Conclusion

In conclusion, I find it vital to make more MS-spectral analysis for more organic compounds and touch on all kinds of mechanisms that lead to various fragmentations. As you can see, the presented work only covered three typed includes alpha, beta, and Retro Diels Alder fragmentations. There are others such as McLafferty Rearrangements, Two-Bond Cleavage, and other special cleavages for alcohols and some compounds-containing carbonyl groups.

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