

CHEM 22100 (Organic Chemistry II) Notes

Steven Labalme

January 19, 2022

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Week 1

Review and Intro to NMR

1.1 Introduction and Review

- 1/11:
- We're skipping alcohols and ethers and coming back later because that's what third quarter really focuses on.
 - What you need to worry about is class content — if he doesn't mention it, even if it's in the book, we won't be responsible for it on exams.
 - Natural products inspire new drugs.
 - Salicylic acid mediates pain, but it will erode the lining of your stomach.
 - Hoffmann functionalizes the alcohol to an ester, removing the negative effects and creating aspirin.
 - Sucrose (table sugar) is glucose plus fructose. Glucose tastes slightly less sweet, and fructose tastes a whole lot sweeter.
 - We now consume 120 pounds of sugar per person per year, different from 20 pounds per person per year in 1976 and 1 pound per person per year in older times.
 - So we have developed artificial sweeteners that cut calories, such as saccharin, aspartame, and sucralose.
 - Sucralose is thermally stable (you can bake with it), has no chloric content, and is made from sugar by protecting some alcohols and replacing others with chlorines.
 - Capsaicin (spiciness) evolved to prevent bugs from biting their host plants.
 - Both capsaicin and resiniferatoxin have the same vanillin group; thus, this group is probably important for reacting with pain receptors.
 - Compactin from mushrooms lowers cholesterol.
 - Zocor and lipitol are derived from it!
 - Taxol (breast cancer treatment) accumulates slowly in rare trees.
 - We can derive from the needles (a renewable resource), however, a compound that is easily functionalized to taxol.
 - It is essential to understand the mechanisms in this course!
 - We won't have to worry much about competing reactivity, but we do need to know how reactivity can change in different situations.
 - Quinine treats malaria.

- Quinine is what makes fizzy water taste bitter.
- In trying to fabricate Quinine, Perkin discovers a compound that dyes fabric purple. Never gets his PhD but makes millions off of this invention. Before, only royals could wear purple (the sole source was mediterranean sea slugs).
- Identify S_N1 by the fact that all chiral information in the reactant will be lost.
- Identify S_N2 by the inversion of stereochemistry.
- We won't worry much about $E1$ this quarter.
- We'll see a lot of $E2$ this quarter.
- We'll look into radical and pericyclic (Diels-Alder) reactions this quarter.
- Molecules that may look similar can actually be quite different.
- Color is related to the number of double bonds in a molecule.
- Blue lobsters are blue because they have enough of an enzyme to sequester all of the colorant in the shells of the lobsters.
 - Would you pay more for it because of its rare color? Probably shouldn't because cooking it will still make it red. It won't taste any better.
- Fleming and penicillin.
 - Initially we have no idea what its structure is.
 - It's hard to synthesize something if we have no idea what it is.
 - During WWII, American and Britain embark on a campaign to synthesize penicillin equal in scope to the Manhattan project, but it wasn't successful.
 - Eventually, Dorothy Crowfoot Hodgkin gets its structure with x-ray crystallography, after wrong attempts from R. B. Woodward and Sir Robert Robinson (future Nobel laureates who hated each other).
 - The moldy cantaloupe.
 - In 1955, John Sheehan at MIT comes up with the first chemical reagent capable of synthesizing penicillin's 4-membered ring.
 - But we made too many antibiotics and antibiotic resistance developed.
 - MRSA is only killed by vancomycin, but they're even developing resistance to that.
 - Thinking chemically to get off the pesticide treadmill.
 - We need the sophistication of nature to build molecules more complex than we can build en masse pharmaceutically.
 - As species go extinct, though, we are losing potential weapons.
- X-ray crystallography pinpoints the location of all atoms other than hydrogen in a molecule.
- Line-angle is gonna be big this quarter.
- We will not be tested on IUPAC nomenclature, but we should know it just to be able to communicate.
- Talks about resonance and induction.
- The IR spectroscopic signal of a carbonyl is 1700 cm^{-1} .
- Resonance affects acidity and IR spectroscopy — bonds that resonate (have less double bond character) will have lower IR frequencies.
- A lot of reactions are quenched by an H_3O^+ workup — just enough to quench, not enough to react.

1.2 Office Hours (Snyder)

- Reviews degrees of unsaturation.
- Talks about resonance, too.
- Make sure you know your functional groups!
- Alkene-based reactions are the most important to review.
- Glucose and mannose are diastereomers.
- Global vs. local symmetry.
 - Helps you determine how many signals you will see in a ^{13}C NMR spectrum.
 - Acetone only has 2 ^{13}C NMR signals (the methyl and the carbonyl one).
 - The ability to draw a mirror plane tells you that certain signals are equivalent.
 - You can rotate hexane into a conformation in which it will have a mirror plane.

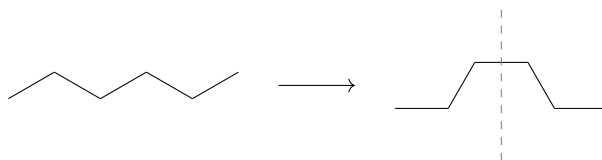


Figure 1.1: Mirror plane in hexane.

- No symmetry, such as in 1-bromo-2,5-dichloro-3,4,6-trimethylbenzene, means all (nine) distinct signals.
- Local symmetry (think an isopropyl group).
 - Look for branch points.
 - You must have consistency of structure for the entirety of branches.
- para-dibromobenzene has only 2 signals since it has *two* mirror planes.

1.3 NMR

- 1/13:
- He is going to try and present a different perspective from the book because otherwise, why take the class.
 - There is no preset curve for this class — everyone can get an A.
 - The right and left boards will be there for the whole class, every class.
 - H_3O^+ workup.

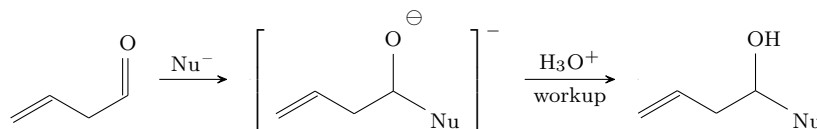


Figure 1.2: H_3O^+ workup.

- Don't think acid-catalyzed hydration. Acid-catalyzed hydration is a very specific reaction. Organic chemists don't really use it because those conditions are so acidic that no other functional groups survive it.

- An H_3O^+ workup is adding H_3O^+ at the end of a reaction to neutralize the structure and excess nucleophile in solution without affecting other groups.
- Next three lectures: Tools for characterizing molecules, e.g., determining what we have in solution.
- It could take decades or even centuries to determine the structure of molecules in the early days of chemistry.
 - It would also take large quantities for experiments.
 - Now we can determine the structures of quantities we can only isolate milligrams of.
- IR can only identify the presence of some functional groups and maybe the identity of a compound that's already been determined (i.e., from the fingerprint region and an online database).
- NMR.
 - Such machines exist in hospitals as MRI.
 - We have dropped the “N” in NMRI because of nuclear’s negative connotation, even though MRI machines have nothing to do with radioactivity.
- Any nucleus that has an odd atomic number will have a dipole moment.
 - The four most significant ones for organic chemistry are ^1H , ^{13}C , ^{15}N , and ^{17}O .
 - The last three are all not commonly occurring isotopes. Oxygen, especially, can barely be measured. Hydrogen will be the most useful because ^1H is the most commonly occurring isotope.
 - For ^{13}C , we will need a longer experiment since only 1/1000 carbon atoms is ^{13}C .
- Theory-lite for NMR.
 - Parallel spins are lower energy, but the difference in energy from anti-parallel is very small (approximately 5×10^{-6} kcal/mol).
 - 1 – 20 mg of compound is needed in 0.75 mL of solvent.
 - This is a non-destructive process — we can recover our compound after running the experiment.
 - We typically use CDCl_3 as our solvent.
 - A part per million (ppm) is a Hz/MHz.
- George Van Dyke Tiers, a grad student at UChicago, determined in 1958 that TMS might be the best standard (low chemical shift, chemically inert, easily removed, etc.).
- Goes over examples from office hours.
- DEPT: Changes the angle of the magnetic field to distinguish CH, CH_2 , and CH_3 groups.
 - DEPT 90 changes the angle by 90° ; DEPT 135 by 135° .
 - In DEPT 90, we’ll only see CH carbons.
 - In DEPT 135, CH and CH_3 groups will peak in the positive direction, and CH_2 groups will peak in the negative direction.
 - Neither experiment will show carbons that aren’t bonded to any hydrogens.

1.4 Chapter 9: Nuclear Magnetic Resonance and Mass Spectroscopy

From Solomons et al. (2016).

- 1/11:
- **Nuclear magnetic resonance spectrum:** A graph that shows the characteristic energy absorption frequencies and intensities for a sample in a magnetic field. *Also known as NMR spectrum.*
 - The chemical shift of a signal gives important clues about molecular structure (see Table 1.1).

Type of Proton	Chemical Shift (δ , ppm)	Type of Proton	Chemical Shift (δ , ppm)
1° Alkyl, RCH ₃	0.8-1.2	Alkyl bromide, RCH ₂ Br	3.4-3.6
2° Alkyl, RCH ₂ R	1.2-1.5	Alkyl chloride, RCH ₂ Cl	3.6-3.8
3° Alkyl, R ₃ CH	1.4-1.8	Vinylic, R ₂ C=CH ₂	4.6-5.0
Allylic, R ₂ C=CR-CH ₃	1.6-1.9	Vinylic, R ₂ C=CRH	5.2-5.7
Ketone, RCOCH ₃	2.1-2.6	Aromatic, ArH	6.0-8.5
Benzylic, ArCH ₃	2.2-2.5	Aldehyde, RCOH	9.5-10.5
Acetylenic, RC≡CH	2.5-3.1	Alcohol hydroxyl, ROH	0.5-6.0*
Alkyl iodide, RCH ₂ I	3.1-3.3	Amino, R-NH ₂	1.0-5.0*
Ether, ROCH ₂ R	3.3-3.9	Phenolic, ArOH	4.5-7.7*
Alcohol, HOCH ₂ R	3.3-4.0	Carboxylic, RCOOH	10-13*

*The chemical shifts of these protons vary in different solvents and with temperature and concentration.

Table 1.1: Approximate proton chemical shifts.

- “In ¹³C NMR spectroscopy, signal area is not relevant in routine analyses” (Solomons et al., 2016, p. 396).
- **Coupling:** The magnetic effect of nonequivalent hydrogen atoms that are within 2 or 3 bonds of the hydrogens producing the signal that splits individual **signals** into multiple **peaks**. *Also known as signal splitting, signal multiplicity.*
- **Vicinal** (hydrogens): Hydrogens on adjacent carbons.
- **Geminal** (hydrogens): Hydrogens bonded to the same carbon.
 - Coupling occurs between geminal hydrogens in chiral/conformationally restricted molecules, specifically diastereotopic hydrogens.
- Interpreting NMR spectra:
 1. Count the number of signals in the spectrum to determine how many distinct proton environments there are in the molecule.
 2. Use chemical shift tables (such as Table 1.1) to correlate the chemical shifts of the signals with possible structural environments.
 3. Determine the relative area of each signal, as compared with the area of other signals, as an indication of the relative number of protons producing the signal.
 4. Interpret the splitting pattern for each signal to determine how many hydrogen atoms are present on carbon atoms adjacent to those producing the signal and sketch possible molecular fragments.
 5. Join the fragments to make a molecule in a fashion that is consistent with the data.

- The external magnetic field causes the σ (and π , if applicable) electrons in the vicinity of each proton to circulate, producing a small local magnetic field that can serve to either increase or decrease the external magnetic field experienced by the proton.
 - Increasing the effective field causes a larger chemical shift (it takes a higher energy photon/less magnetic field to induce a spin flip).
 - Decreasing the effective field causes a smaller chemical shift (it takes less energy/more magnetic field to induce a spin flip).
- **Shielded** (proton): A proton for which the induced local magnetic field opposes the external magnetic field to a relatively large degree.
- **Deshielded** (proton): A proton for which the induced local magnetic field opposes the external magnetic field to a relatively small degree (or even reinforces the external magnetic field).
 - For example, the π electrons of benzene circulate in such a way that the external magnetic field at the aromatic hydrogens is *augmented*.
- “Chemically equivalent protons are chemical shift equivalent in ^1H NMR spectra” (Solomons et al., 2016, p. 403).
- **Homotopic** (atoms): A set of atoms on some molecule such that replacing different ones with the same group gives the same compound.
 - For example, the six hydrogens of ethane are homotopic since replacing any of them with chlorine (for instance) gives the same compound: chloroethane.
 - Homotopic hydrogens are chemical shift equivalent.
- **Heterotopic** (atoms): A set of atoms on some molecule such that replacing different ones with the same group gives different compounds.
 - For example, in chloroethane, the CH_2 hydrogens are heterotopic to the CH_3 hydrogens since replacing the former yields 1,1-dichloroethane and replacing the latter yields 1,2-dichloroethane.
 - Heterotopic atoms are *not* chemical shift equivalent.
- **Enantiotopic** (atoms): Two atoms on some molecule such that replacing different atoms with the same group gives enantiomers.
 - Example: The CH_2 hydrogens of bromoethane.
 - Enantiotopic atoms are chemical shift equivalent, except possibly when the compound in question is dissolved in a chiral solvent.
- **Diastereotopic** (atoms): Two atoms on some molecule such that replacing different atoms with the same group gives diastereomers.
 - Example: The CH_2 hydrogens of 2-butanol.
 - Diastereotopic atoms are *not* chemical shift equivalent (the asymmetry of the chirality center ensures this), except possibly by coincidence.
- **Coupling constant**: The separation in hertz between each peak of a signal. *Denoted by J .*
 - On the order of 6 – 8 Hz.
- The reciprocity of coupling constants: The coupling constants of coupled atoms are the same.
 - In more complicated molecules, noting that two signals have the same coupling constant means the protons to which they correspond are likely coupled.

- **Dihedral angle** (between vicinal groups): The angle between vicinal groups as seen on the Newman projection through the bond connecting their parent atoms. *Denoted by ϕ .*
- **Karplus correlation**: The dependence of the coupling constant on dihedral angles.
 - Discovered by Martin Karplus of Harvard.
 - Useful for identifying cyclohexane conformations, and thus for determining which conformation is lower energy.
- An NMR spectrometer is a camera with a relatively slow shutter speed, in that it blurs pictures of rapidly occurring molecular processes.
- Examples of rapid processes that occur in organic molecules.
 - Chemical exchanges cause spin decoupling.
 - Consider ethanol.
 - Based on its structure, we'd predict that the signal corresponding to the hydroxyl proton would be a triplet.
 - However, it only appears as a triplet in very pure ethanol, where **chemical exchange** is slower due to the reduction in impurity-assisted chemical exchange catalysis common in normal ethanol.
 - Rapid chemical exchange means that neighboring protons don't have enough time to couple; thus, the hydroxyl proton appears as a singlet in relatively impure ethanol.
 - Occurs in the ^1H NMR spectra of alcohols, amines, and carboxylic acids; the signals of OH and NH protons are normally unsplit and broad.
 - "Protons that undergo rapid chemical exchange... can be easily detected by placing the compound in D_2O . The protons are rapidly replaced by deuterons, and the proton signal disappears from the spectrum" (Solomons et al., 2016, p. 413).
 - Conformational changes.
 - If, for example, we could isolate staggered bromoethane, the CH_3 hydrogens would be split into two signals, as the one anti-periplanar hydrogen is in a different chemical environment from its two geminal neighbors.
 - But we can't, so all three CH_3 hydrogens contribute to one peak.
- **Chemical exchange**: The swapping of identical atoms between molecules.
- **Exchangeable proton**: A proton that can engage in rapid chemical exchange.
- We now switch gears to ^{13}C NMR spectroscopy.
- Although ^{13}C does not occur naturally with nearly the same frequency as ^{12}C , it is important for its application to NMR spectroscopy.
- Simplifications from ^1H NMR spectroscopy.
 - Each distinct carbon produces one signal in a ^{13}C NMR spectrum.
 - Splitting of ^{13}C signals into multiple peaks is not observed in routine ^{13}C NMR spectra.
- No (technically just very little) carbon-carbon coupling since coupling only occurs for adjacent carbons and only 1 in 100 carbon atoms is ^{13}C (1.1 % natural abundance).
- Carbon-proton coupling can occur, however, splitting ^{13}C signals into multiplets.
- **Broadband proton decoupled** (spectrum): A ^{13}C NMR spectrum in which ^1H - ^{13}C coupling is eliminated by choosing instrumental parameters to decouple the proton-carbon interactions. *Also known as BB proton decoupled.*

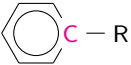
Type of Proton	Chemical Shift (δ , ppm)
1° Alkyl, RCH_3	0-40
2° Alkyl, RCH_2R	10-50
3° Alkyl, RCHR_2	15-50
Alkyl halide or amine, R_3CX ($\text{X} = \text{Cl}, \text{Br}, \text{NR}'_2$)	10-65
Alcohol or ether, $\text{R}_3\text{COR}'$	50-90
Alkyne, $\text{RC}\equiv\text{R}'$	60-90
Alkene, $\text{R}_2\text{C}=\text{R}'$	100-170
Aryl,  $\text{C}-\text{R}$	100-170
Nitrile, $\text{RC}\equiv\text{N}$	120-130
Amide, RCONR'_2	150-180
Carboxylic acid or ester, RCOOR'	160-185
Aldehyde or ketone, RCOR'	182-215

Table 1.2: Approximate carbon-13 chemical shifts.

- Shielding and deshielding works the same way (see Table 1.2).
- In addition to the TMS peak, ^{13}C spectra have a CDCl_3 solvent peak at δ 77.
- **DEPT ^{13}C NMR spectrum:** A ^{13}C NMR spectrum that indicates how many hydrogen atoms are bonded to each carbon, while also providing the chemical shift information contained in a broadband proton-decoupled ^{13}C NMR spectrum. *Also known as distortionless enhancement by polarization transfer.*

Week 2

Spectrometry

2.1 Office Hours (Snyder)

- 1/17:
- Does cyclohexane only have one ^{13}C NMR signal, and only one ^1H NMR signal?
 - 1 singlet for ^{13}C .
 - 1 singlet for ^1H .
 - We don't integrate carbon.
 - We only integrate to compare things.
 - We won't have to deal with cyclohexane conformations wrt. NMR on any test.
 - What do we need to know about the Karplus correlation?
 - We won't need it for problems.
 - It's useful, but we've got other things to worry about.
 - Do chemists/when do chemists run ^{13}C NMR experiments with all carbons isotopically carbon-13?
 - Is the reason we don't integrate carbon because the placing of the carbon-13s is random? Would the proportions not still be representative?
 - For ^1H NMR, feel free to draw in the hydrogen atoms on the line-angle structure.
 - Multiplying $n + 1$ of different types of neighbors (e.g., if a hydrogen has 3 neighboring hydrogens to one side and 2 neighboring hydrogens to the other side, it has a maximum of $(3 + 1)(2 + 1) = 12$ peaks in its signal).
 - The multiplication analysis applies only to chains that are completely different.

2.2 Chapter 9: Nuclear Magnetic Resonance and Mass Spectroscopy

From Solomons et al. (2016).

- 1/18:
- **Mass spectrometry:** The formation of ions in a mass spectrometer followed by separation and detection of the ions according to mass and charge.
 - **Mass spectrum:** A graph that on the x -axis represents the formula weights of the detected ions, and on the y -axis represents the abundance of each detected ion.
 - The x -axis is labeled m/z where m is mass and z is charge.

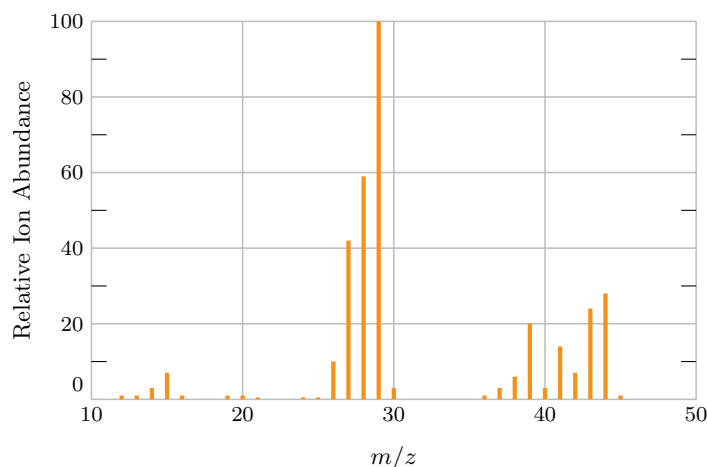


Figure 2.1: The mass spectrum of propane.

- The examples Solomons et al. (2016) consider all have $z = +1$, so the x -axis in them effectively represents the formula weight of each detected ion.
- **Base peak:** The tallest peak in a mass spectrum.
 - Relative ion abundance on the y -axis is either expressed as a percentage of the base peak or directly as the number of detected ions.
 - Usually an easily formed fragment of the original compound.
 - The base peak in Figure 2.1 corresponds to the C_2H_5^+ ion, $m/z = 29 = 2 \cdot 12 + 5 \cdot 1$.
- **Molecular ion:** The ion with the formula weight of the original compound.
 - One of the higher value m/z peaks.
 - Usually not the base peak.
- Small peaks having m/z values 1 or 2 higher than the formula weight of the compound are due to ^{13}C and other isotopes.
- **Electron impact:** A method for ionizing molecules in a mass spectrometer by placing the sample under high vacuum and bombarding it with a beam of high-energy electrons. *Also known as EI.*
 - The energy of the electrons is in the range of 70 eV or 6.7×10^3 kJ/mol.
 - The incoming electrons ionize the molecules to molecular ions, which are radical cations since they have a +1 charge and an unshared electron.
- Note that there are ionization methods other than EI, but it is the most common.
- Localizing the radical and charge along the structure.

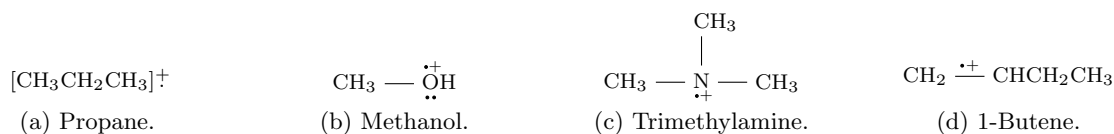


Figure 2.2: Molecular ions.

- The choice of where we localize the radical/charge is often arbitrary (esp. with hydrocarbons).

- However, “as we might expect, ionization potentials indicate that in [the] formation of radical cations, the nonbonding electrons of nitrogen, oxygen, and halogen atoms, and the π electrons of alkenes and aromatic molecules, are held more loosely than the electrons of carbon-carbon and carbon-hydrogen σ bonds” (Solomons et al., 2016, p. 425).
- Thus, “when a molecule contains oxygen, nitrogen, or a π bond, we place the odd electron and charge at a nitrogen, oxygen, halogen, or π bond. If resonance is possible, the radical cation may be delocalized” (Solomons et al., 2016, p. 425).
- Three important principles.
 1. The reactions that take place are all unimolecular since the pressure is kept so low.
 2. Single-barbed arrows denote the movement of single electrons.
 3. The relative ion abundances give key information about the structures of the fragments produced and their original locations in the molecule.
- Fragmentation by cleavage at a single bond.
 - When such a process happens in a molecular ion, a cation and a radical are produced, although only the cation will be detected by the positive ion mass spectrometers we’re considering.
 - Each cleavage can happen in two ways (since one fragment will take the radical and the other will take the positive charge).
 - The path that produces the more stable carbocation will occur more rapidly.
 - Notice the difference in relative ion abundance between the secondary CH_3CH_2^+ ($m/z = 29$) and the primary CH_3^+ ($m/z = 15$) in Figure 2.1.
- When drawing cleavage reactions, use brackets and delocalization; when drawing cleavage mechanisms, use localization.
- Chain branching increases the likelihood of cleavage at a branch point because a more stable carbocation can result.
- Examples of fragmentation to form resonance-stabilized cations.
 1. Alkenes ionize and frequently undergo fragmentations that yield resonance-stabilized allylic cations.

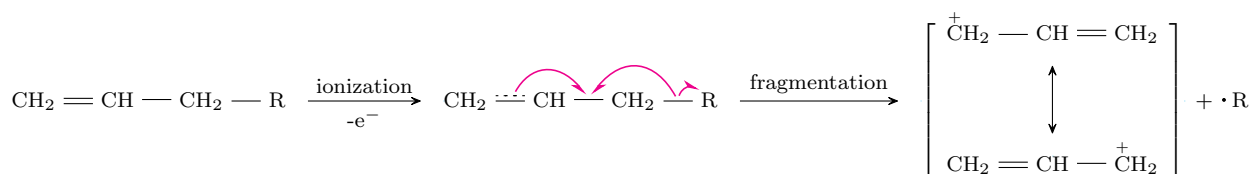


Figure 2.3: Resonance fragmentation: Alkenes.

2. Carbon-carbon bonds next to an atom with a lone pair usually break readily because the resulting carbocation is resonance stabilized.

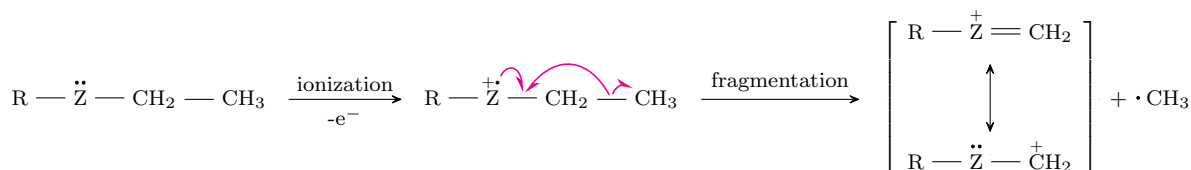


Figure 2.4: Resonance fragmentation: Lone pairs.

3. Carbon-carbon bonds next to the carbonyl group of an aldehyde or ketone break readily because resonance-stabilized ions called **acylium ions** are produced.

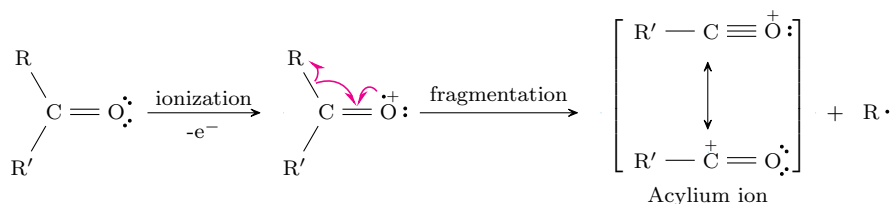
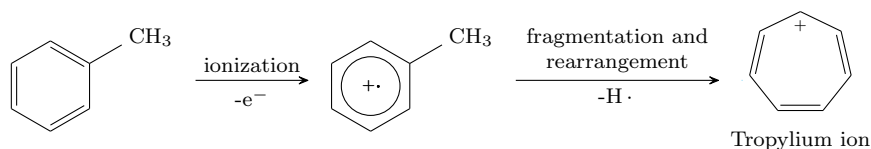


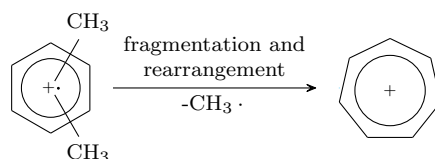
Figure 2.5: Resonance fragmentation: Carbonyls.

– Note that either the C–R or the C–R' bond could break.

4. Alkyl substituted benzenes ionize by loss of a π electron and undergo loss of a hydrogen atom or methyl group to yield the relatively stable **tropylium ion**. This fragmentation gives a prominent peak (sometimes the base peak) at $m/z = 91$.



(a) Losing a hydrogen radical.



(b) Losing a methyl radical.

Figure 2.6: Resonance fragmentation: Alkyl-substituted benzene rings.

5. Monosubstituted benzenes with other than alkyl groups also ionize by loss of a π electron and then lose their substituent to yield a phenyl cation with $m/z = 77$.

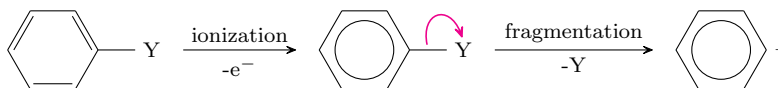
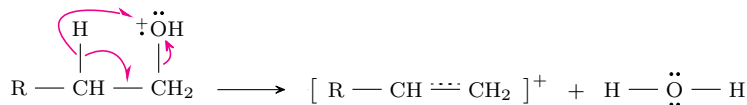


Figure 2.7: Resonance fragmentation: Monosubstituted benzene rings with nonalkyl groups.

– Y is a halogen, nitro group, acyl group, nitrile group, etc.

- Fragmentation by cleavage of two bonds leads to a new radical cation and a neutral molecule.

1. Alcohols frequently show a peak at $M^+ - 18$. This corresponds to the loss of a molecule of water.

Figure 2.8: Fragmentation: Loss of H_2O .

2. Carbonyl compounds with a hydrogen on their γ carbon undergo a fragmentation called the McLafferty rearrangement.

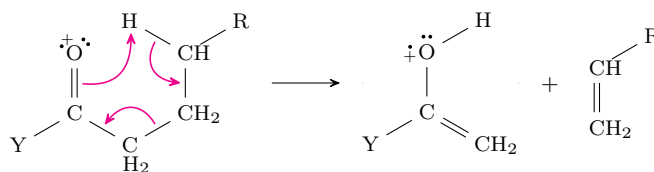


Figure 2.9: Fragmentation: McLafferty rearrangement.

- Y may be an alkyl, hydride, ether, hydroxyl, etc.
3. There are also often peaks corresponding to the elimination of other small molecules.
- Isotope effects:
 - The presence of ^{13}C will provide a small peak at $M^+ + 1$.
 - “In the mass spectrum for a sample containing chlorine, we would expect to find peaks separated by two mass units, in an approximately 3 : 1 (75.5% : 24.5%) ratio for the molecular ion or any fragments that contain chlorine” (Solomons et al., 2016, p. 432).
 - “In the mass spectrum for a sample containing bromine, we would expect to find peaks separated by two mass units in an approximately 1 : 1 ratio (50.5% : 49.5% ^{79}Br to ^{81}Br)” (Solomons et al., 2016, p. 433).
 - In a molecule containing two bromine atoms, for example, we’ll see peaks at M^+ , $M^+ + 2$, and $M^+ + 4$ in a 1 : 2 : 1 ratio.

References

Solomons, T. W. G., Fryhle, C. B., & Snyder, S. A. (2016). *Organic chemistry* (12th). John Wiley & Sons.