

2.4: Functional groups containing sp²-hybridized heteroatom

Learning Objectives

- Identify, given IUPAC names to the structural formula, and draw the structural formula from the IUPAC name of simple aldehydes, ketones, and imines.
- Understand the polarity and predict some physical properties, reactive sites, and relative reactivities of aldehydes, ketones, and imines based on the bond polarity.

Carbonyl group and its subclasses

A (C=O) group is a carbonyl group. It has a σ -bond between sp² orbitals and a π between p orbitals of a C and an O. Lone pairs of electrons occupy the remaining two sp² orbitals of O as shown here: $\text{C}=\ddot{\text{O}}:$. The lone pairs are usually not shown. The

carbonyl group is represented as $\text{C}=\text{O}$, $\text{C}=\ddot{\text{O}}$ or simply as $\text{C}=\text{O}$. If the O is replaced with N it becomes an imine $\text{C}=\text{NR}$ group.

The carbonyl group is subdivided into aldehydes, ketones, carboxylic acids, and carboxylic acid derivatives based on what is bonded to the carbonyl carbon, i.e., what are the X and Y in this formula: $\text{X}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{Y}$, as listed in Table 1.

Table 1: Sub-groups of carbonyl group based on what is X and Y in the general formula of a carbonyl group: $\text{X}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{Y}$.

X	Y	Group name	General formula
Hydrocarbon (R) or H	H	Aldehyde	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{H}$
Hydrocarbon (R)	Hydrocarbon (R')	Ketone	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{R}'$
Hydrocarbon (R) or H	NR $-\text{C}-\text{R}''$	Imine	$\text{R}'-\overset{\text{NR}}{\underset{\text{ }}{\text{C}}}-\text{R}''$
Hydrocarbon (R) or H	Alcohol group ($-\text{OH}$)	Carboxylic acid	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{OH}$
Hydrocarbon (R) or H	Oxy anion ($-\text{O}^-$)	Carboxylate anion	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{O}^-$
Hydrocarbon (R) or H	Halogen ($-\text{X}$, where $-\text{X} = -\text{F}, -\text{Cl}, -\text{Br}, \text{ or } -\text{I}$)	Acid halide	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{X}$
Hydrocarbon (R) or H	$\text{Carboxyl } (-\text{O}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{R}')$	Acid anhydride	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{O}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{R}'$
Hydrocarbon (R) or H	Alkoxy ($-\text{OR}'$)	Ester	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{OR}'$
Hydrocarbon (R) or H	Amine ($-\text{NH}_2$, $-\text{NHR}'$, or $-\text{NR}'\text{R}''$)	Amide	$\text{R}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{NH}_2$
Hydrocarbon (R)	Cyano ($-\text{C} \equiv \text{N}$)	Nitrile	$\text{R}-\text{C} \equiv \text{N}$

The first three, i.e., aldehydes, ketones, and imines, are described in this section. The others, i.e., carboxylic acids and their derivatives, including carboxylate anion, acid anhydrides, acid halides, esters, and amides, are described in the next section. The nitrile group is classified as a carboxylic acid derivative.

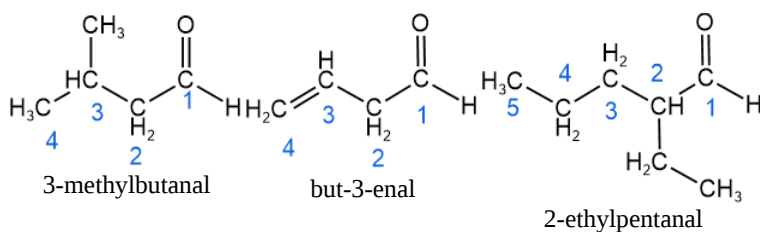
Aldehydes

An aldehyde has either two H's or a H and a hydrocarbon R single bonded with the carbonyl carbon, i.e., $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ group. The condensed form of the aldehyde group is $-\text{CHO}$.

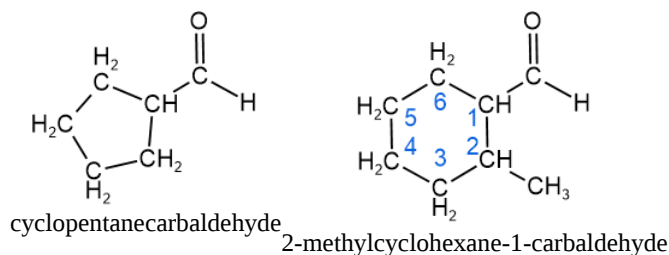
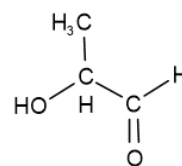
Nomenclature of aldehydes

The IUPAC naming of aldehydes follows the rules of naming alcohols, with the following changes.

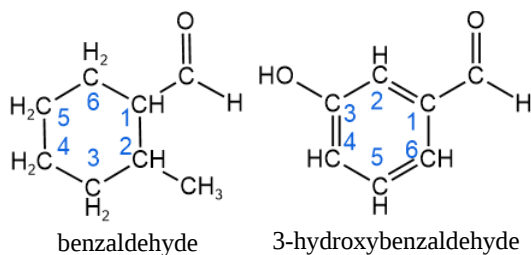
- The longest chain **containing the aldehyde group** is chosen as the parent name with the last 'e' of the suffix replaced with -al, e.g., CH_3CHO is ethanal.
- Start numbering from the aldehyde C. If there is one aldehyde group, it is understood to be #1, i.e., no need to show the number. A few examples are shown below.



- If more than one functional groups are present, the order of preference of functional groups is the following: $\text{carboxylic acid} > \text{aldehyde} > \text{ketone} > \text{alcohol} > \text{amine} > \text{thiol}$. A suffix represents the higher priority group, and prefixes represent the other groups. For example, 2-hydroxypropanal shown on the right.
- The suffix "carbaldehyde" represents an aldehyde group bonded to a cycloalkane. Numbering starts from the point of attachment of the aldehyde to the cycloalkane, as shown in the examples below.



- An aldehyde group bonded to a benzene ring has the parent name benzaldehyde, as shown in the following examples. Numbering, if needed, starts from the aldehyde attachment point.



The common name of methanal ($\text{H}_2\text{C}=\text{O}$) is formaldehyde, and ethanal (CH_3-CHO) is acetaldehyde. Aldehydes take their common names from the common names of carboxylic acids, described in a later section.

✓ Example 2.4.1

What is the IUPAC name of this compound shown in the figure on the right?

Solution

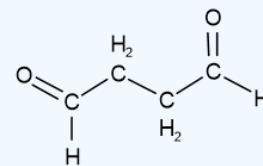
the longest chain containing aldehyde groups is four C, i.e., butane.

Change the final 'e' with -al, and since there are two aldehyde groups, use dial.

Answer: butanedial

Note 1: the final 'e' is dropped when the following letter added starts with a vowel, e.g., -al; otherwise, it is retained as in butanedial.

Note 2: Location number is not needed even for this dialdehyde because it is understood that the aldehyde groups are at the end of the chain.



✓ Example 2.4.2

What is the IUPAC name of this compound shown in the figure on the right?

Solution

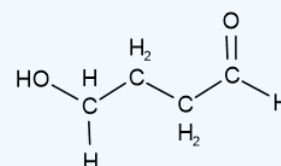
The longest chain is four C, i.e., butane

There is an aldehyde group, so change the final 'e' with -al, i.e., butanal.

There is an alcohol group that is added as a hydroxy- prefix, i.e., hydroxybutanal.

The alcohol group needs the location number, start from aldehyde, and the alcohol group receives #4.

Answer: 4-hydroxybutanal.



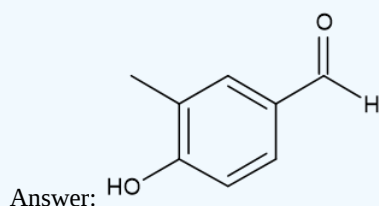
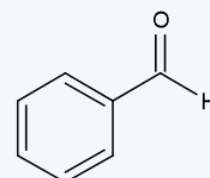
✓ Example 2.4.3

Write the skeletal formula of 4-hydroxy-3-methylbenzaldehyde?

Solution

The parent name is benzaldehyde, i.e., an aromatic ring with an aldehyde group as shown on the right.

Start the number from the point of attachment of aldehyde and go either clockwise or counterclockwise and place a methyl group at #3 and an alcohol group at #4.



Physical properties of aldehydes

The aldehydes have sp^2 -hybridized C and O with a double bond (a σ and a π -bond) between them, two lone pairs occupying two sp^2 -orbital of an O, and the C bonded with a H and a hydrocarbon R or another H, i.e., $-C=\ddot{O}:$. The C=O bond is polar, i.e.,

$\delta^+ \delta^-$
 $C=O$, because O are more electronegative than C ($3.3-2.1 = 0.9$), as shown in Figure 2.4.1. It makes the C a δ^+ , i.e., an electrophile in reactivity and the O a δ^- , i.e., a nucleophile or a base in reactivity. The lone pair of electrons on O add to the base character of the carbonyl O.

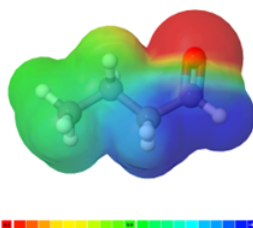
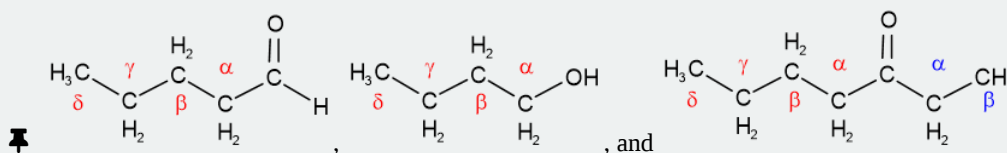


Figure 2.4.1: Electrostatic potential map of butanal ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$). C's are gray, H's are white and O is red in the model. Blue region is δ^+ , red is δ^- , and green is neutral. (Copyright; Public domain)

Note that the δ^+ region extends from carbonyl C to the C attached to it, designated as αC and the H's on the αC .

✚ α -, β -, γ -, δ - designations of C's

The C directly bonded to a functional group is designated as ✚ α , the next one as β , the third as γ , and so on. A few examples are shown below for explanation.



Aldehyde group ($\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$) is polar. Aldehydes have boiling points higher than the alkanes of comparable molar mass due to the dipole-dipole interaction in addition to London dispersion forces. Aldehydes have boiling points lower than alcohols of the comparable mass because aldehydes do not have hydrogen bonding with each other, as compared below.

Name	Condensed formula	Molar mass	Boiling point
Pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	72 g/mol	36 °C
Butanal	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	72 g/mol	76 °C
Butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	74 g/mol	117 °C

Aldehydes can establish hydrogen bonding with water molecules through $\overset{\delta-}{\text{O}}$ of carbonyl group with $\overset{\delta+}{\text{H}}$ of water molecules. Therefore, aldehydes up to four C's, i.e., methanal, ethanal, propanal, and butanal, are soluble in water. Pentanal with five C's is slightly soluble, and hexanal with six C's is insoluble. Aldehydes, except for formaldehyde, generally smell pleasant and are used in perfumes.

Ketones

A ketone has two hydrocarbon groups bonded with the carbonyl carbon, i.e., $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$ group. The condensed form of the aldehyde group is RCOR' .

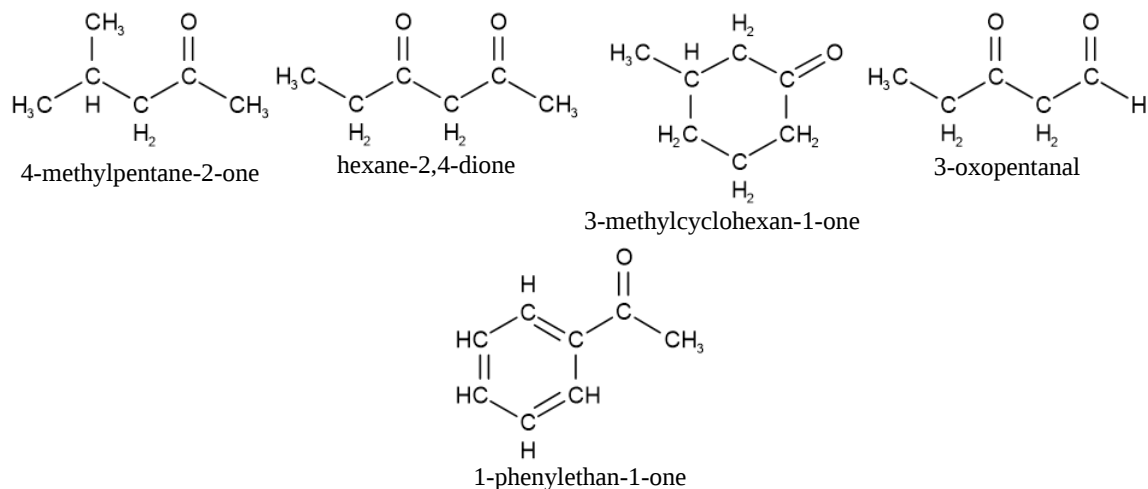
Nomenclature of ketones

The IUPAC naming of ketones followed the rules of naming alcohols and aldehydes, summarized below.

- The longest chain **containing the ketone group** is chosen as the parent name, with the last 'e' of the suffix replaced with -one.
 - The parent chain is numbered starting from the end, which gives the lower number to the ketone group, e.g., CH_3COCH_3 is propan-2-one.
 - For two ketone groups -dione and three -trione suffix is used.
 - For cyclic ketones, the parent name of cycloalkane is used with the last 'e' replaced with -one. Some examples are shown below.

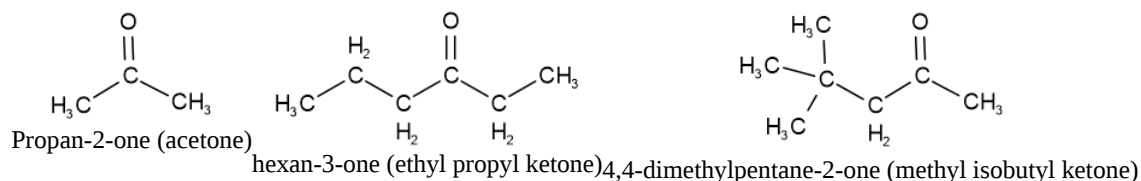
- If a group of higher precedence, e.g., an aldehyde, is also present, then ketone is represented by the prefix -oxo, as shown below.
- A benzene ring is represented by the prefix phenyl-, as shown below.

Some examples of the naming using the above rules are shown below.



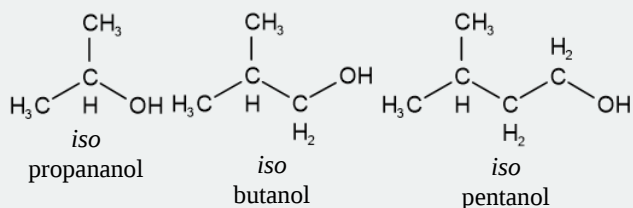
Common names of ketones

Propan-2-one is acetone, and 1-phenylethan-1-one is acetophenone. Common names of other ketones are obtained by listing the alkyl groups bonded to the carbonyl group in the order of group size, followed by the word ketone, as shown below with common names in brackets.



Iso-Group

An alkyl group containing $-\text{CH}_3$ attached to the 2nd last *ceC* takes iso- prefix, as shown in the examples below.



The group names with iso-prefix are often used in common names and are also accepted in IUPAC nomenclature.

✓ Example 2.4.1

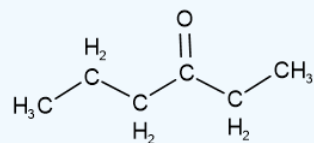
What is the IUPAC name of this compound shown in the figure on the right?

Solution

the longest chain containing ketone groups is six C, i.e., hexane.

Change the final 'e' with -one, i.e., hexanone.

Add the location of the ketone group. Start numbering the parent chain from the end, giving the ketone a lower number. Ketone receives #3



Answer: hexan-3-one

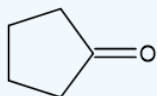
✓ Example 2.4.2

Write the skeletal formula of cyclopentanone.

Solution

The parent name is cyclopentane as shown in the figure on the right.

Add a ketone group to any carbon.



Answer:

✓ Example 2.4.3

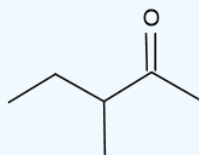
Write the skeletal formula of 3-methylpentane-2-one?

Solution

Parent name is pentane:



Count from either side and add a carbonyl group to C#2 and a methyl group to C#3.



Answer:

Physical properties of Ketones

Ketones have sp^2 -hybridized C and O with a double bond (a σ and a π -bond) between them, two lone pairs occupying two sp^2 -

orbital of an O, and the C bonded with two hydrocarbon groups. i.e., $R-\overset{\text{:O:}}{\underset{\text{||}}{C}}-R'$. The C=O bond is polar, i.e., $\overset{\delta+}{C}=\overset{\delta-}{O}$ because O are more electronegative than C ($3.3-2.1 = 0.9$), as shown in Figure 2.4.2. It makes the C a δ^+ , i.e., an electrophile in reactivity and the O a δ^- , i.e., a nucleophile or a base in reactivity. The lone pair of electrons on O add to the base character of the carbonyl O.

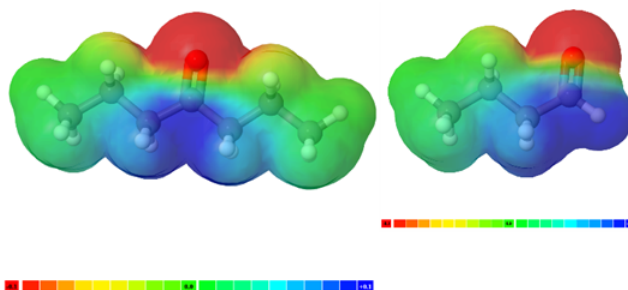


Figure 2.4.2: Electrostatic potential map of a ketone compared with an aldehyde. Haptan-4-one ($CH_3CH_2CH_2COCH_2CH_2CH_3$) and Butanal ($CH_3CH_2CH_2CHO$). C's are gray, H's are white, and O is red on the model. Blue region is δ^+ , red is δ^- , and green is neutral. (Copyright; Public domain)

Comparison of carbonyl C of an aldehyde and a ketone

Figure 2.4.2 compares the electrostatic potential maps of an aldehyde and a ketone. The following are the points to note:

- The carbonyl C is more $\delta+$ in an aldehyde than in a ketone. The reason is that the alkyl group of ketone partially neutralizes the $\delta+$ of the carbonyl C by hyperconjugation while the H of the aldehyde can not. (Note: hyperconjugation is a special form of resonance which involves σ -bonds. The details of it are out of the scope of this book)
- The carbonyl C of an aldehyde is more accessible to reagents in chemical reactions than the carbonyl C of a ketone. This is because H in an aldehyde is small compared to the hydrocarbon group in a ketone.

These two factors make an aldehyde a more reactive electrophile than a ketone.

Other than the reactivity difference between an aldehyde and a ketone described above, the physical characteristics, i.e., the trend in the boiling points, solubility in water, etc., are the same for aldehydes and ketones.

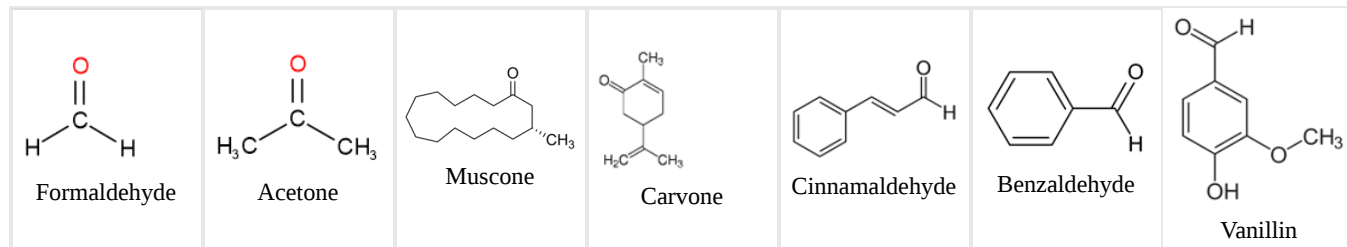
Some important aldehydes and ketones

Aldehydes and ketones are often part of the biochemical processes. They are often an intermediate in the conversion of food into energy.

Methanal or **formaldehyde** is a colorless gas with pungent odor that has germicidal properties. A 40% mixture of formaldehyde in water called formalin is used to preserve biological specimens. Formaldehyde is a starting material of polymers used in fabrics, insulation, carpeting, and other products.

Propan-1-one, or **acetone**, is a colorless liquid with a mild odor used as a solvent in paints, nail polish removers, rubber cement, and cleaning fluids. Care must be taken in handling acetone as it is highly volatile and flammable.

Several natural products are aldehydes or ketones used to flavor foods or as components of fragrances. For example, muscone is a ketone used in musk perfumes. Oil of spearmint contains carvone which is a ketone; cinnamaldehyde is found in cinnamon, almonds contain benzaldehyde, and vanillin is found in vanilla beans. The structures of these aldehydes and ketones are shown below.

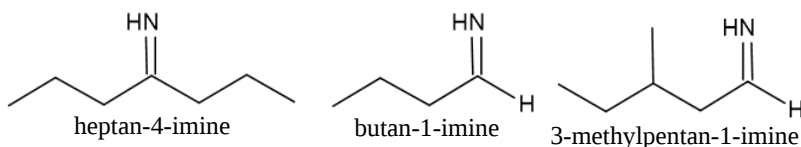


Imines

Replacing carbonyl O with a N in a carbonyl ($C=O$) makes an imine group, i.e., $R'-C(=NR)''$. Note that N has three bonds and one lone pair. The third bond of N is with a H or a hydrocarbon (R) in this case. Imines are less common but important as reactive intermediates.

Nomenclature of imines

IUPAC rules for naming imines are the same as for the corresponding aldehydes or ketones, except that the -al or -one is replaced with the suffix -imine, as shown by the examples below.



Physical properties of imines

The C=N bond is polar, i.e., $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{N}}$ because N are more electronegative than C ($3.0-2.5 = 0.5$), as shown in Figure 2.4.4. It makes the C a δ^+ , i.e., an electrophile in reactivity and the N a δ^- , i.e., a nucleophile or a base in reactivity. The lone pair of electrons on N add to the base character of the N in an imine group.

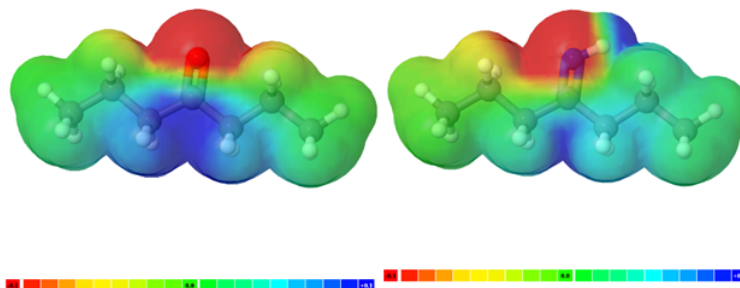


Figure 2.4.3: Electrostatic potential map of a ketone and imine are compared. Haptan-4-one ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$), and haptan-4-imine ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CNHCH}_2\text{CH}_2\text{CH}_3$). C's are gray, H's are white O is red and blue is N in the model. Blue region is δ^+ , red is δ^- , and green is neutral. (Copyright; Public domain)

A comparison of the electrostatic potential map in Figure 2.4.3 shows that the C of an imine group is much less δ^+ than the corresponding carbonyl C (notice a less blue area in the case of imine compared to the corresponding ketone). This is because C=O bond is more polar ($3.5-2.5 = 1.0$) than a C=N bond ($3.0-2.5 = 0.5$). Based on the less polar bond, one would expect imines to be more stable in chemical reactions than the corresponding aldehydes or ketones. Since N is less electronegative, it holds on to the lone pair less tightly than an O, which makes imine more basic, i.e., they easily donate their lone pair to a proton. Once the N makes the bond with a proton, it becomes positive charge species that is more reactive than the carbonyl compound it is derived from. Imines are less common but more important as reactive intermediates in converting aldehydes and ketones, particularly in biochemical systems.

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