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SELF.ORG.CHEM

INTRODUCTION TO

# ***FUNCTIONAL GROUPS OF ORGANIC COMPOUNDS***

***21 SLIDES, 60-90 MINUTES***

***LEVEL: BASIC***

code *Bofg1TW*

Prof. M. E. Alonso-Amelot

## ***GUIDANCE SCRIPT FOR LECTURER & COMPLEMENTARY MATERIAL FOR STUDENTS***

*For instructions to better use this material go to page 32*

### **IN THIS LECTURE:**

Carbon in organic compounds exists in many forms depending on how it is associated with other atoms. These atom associations constitute the *functional groups*.

This lecture has been designed for beginning students (1<sup>st</sup> semester) who need to become familiar with the most important functional groups of organic compounds. They are an essential part of the chemical language.

These functions are reviewed according to a plan based on two lines of reasoning:

- 1.- Number and type of substituents
- 2.- Number of atoms (one to four) and type of bond ( or ) to these other atoms.

Functional groups are organized accordingly. Although memorization is unavoidable, the systematic construction of these functions alleviates the burden of remembering structures and nomenclature.

## **SLIDE 2**

### **LECTURE CONTENTS:**

- 1.- [Why is this topic so important?](#)
- 2.- [What is a functional group?](#)
- 3.- [The most common functional groups you cannot do without.](#)
- 4.- [Approaching functional groups systematically.](#)
- 5.- [The fundamental structures around C.](#)
- 6.- [A quick view of functional groups associated with each structural type.](#)
- 7.- [Functional groups of the C=C and C≡C types.](#)
- 8.- [Functional groups of the C-X type.](#)
- 9.- [Functional groups of the C-X-X type.](#)
- 10.- [Functional groups of the C-X=Y type.](#)
- 11.- [Functional groups of the X-C-Y type.](#)
- 12.- [Functional groups of the C=X type.](#)
- 13.- [Functional groups of the Y-C=X type.](#)
- 14.- [Functional groups containing three heteroatoms.](#)
- 15.- [The Z-C≡X and Z=C=X types.](#)
- 16.- [All types in one quick view.](#)

All these topics appear in condensed form on the menu slide.

**SLIDE 3*****WHY THIS TOPIC IS SO IMPORTANT***

Functional groups, as the name suggests, concentrate most of the reactivity of organic molecules. Therefore, recognizing the reactive centers from their molecular looks and associate them with familiar names is part of the essential language required of any organic chemist.

**SLIDE 4****WHAT IS A FUNCTIONAL GROUP**

A functional group may be defined in various ways. A couple of good ones:

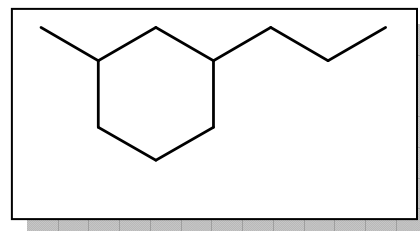
☞ *A collection of atoms that participate in organic reactions*

☞ *A cluster of atoms in the molecule where reactions are more likely to take place.*

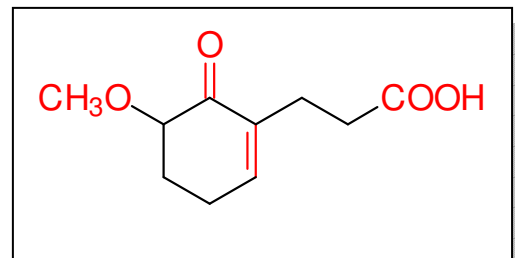
In our opinion, the later suits better the operative definition. However, there are uncommon instances where this is not entirely true: remote group activation reactions and free radical processes in hydrocarbons.

The point here is that functional groups are the place you should concentrate your attention when confronted with a molecular structure at the time of studying its chemical properties and reactivity.

Suppose that you have a certain carbon skeleton. There are no functional groups, all you have is saturated carbons, CH, CH<sub>2</sub> and CH<sub>3</sub>. For chemical reactions to take place here one must use considerable heat and highly reactive species such as free radicals.



Adding functional groups to this carbon backbone lowers enormously the energy barriers of chemical processes. This means much lower temperatures, even as low as  $-78^{\circ}\text{C}$ , and access to a gamut of thousands of different reagents widely used in organic synthesis.



Functional groups may occur in two general sets relative to the molecular backbone:

- 1.- As substituents bonded to the carbon chain. They replace a C-H bond
- 2.- As part of the molecular backbone, embedded in the carbon chains.

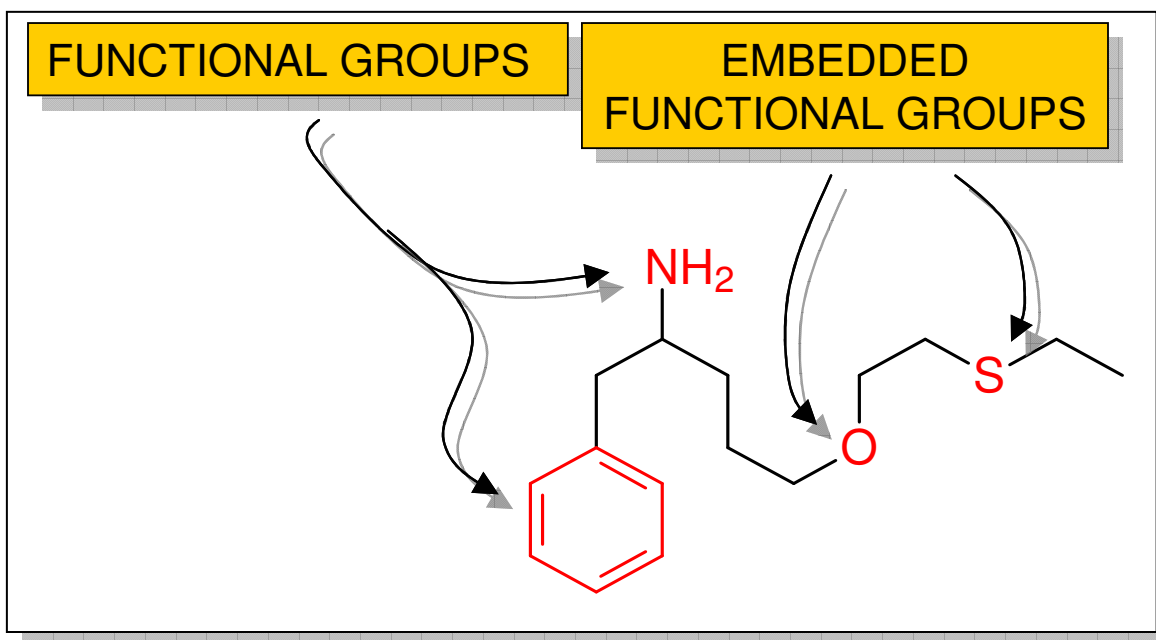


Figure 1: Functional groups are of two general types: 1) those replacing H atoms in C chains or cycles, and 2) embedded within the chain or cycle

Depending strongly on their position in the molecular frame, the functional groups will interact (react) with other reactive compounds in the medium as well as with solvent molecules, catalysts, molecules of itself and even other atoms within the same molecule through attractive or repulsive forces. Such interference may be crucial in guiding a reaction course.

### **SLIDE 5**

#### **THE MOST COMMON FUNCTIONALITIES**

There are scores of functional groups in organic compounds. However, there are a few you cannot live without. As a fast track introduction to this extensive topic, consider the following list you ought to become familiar with, no matter what.

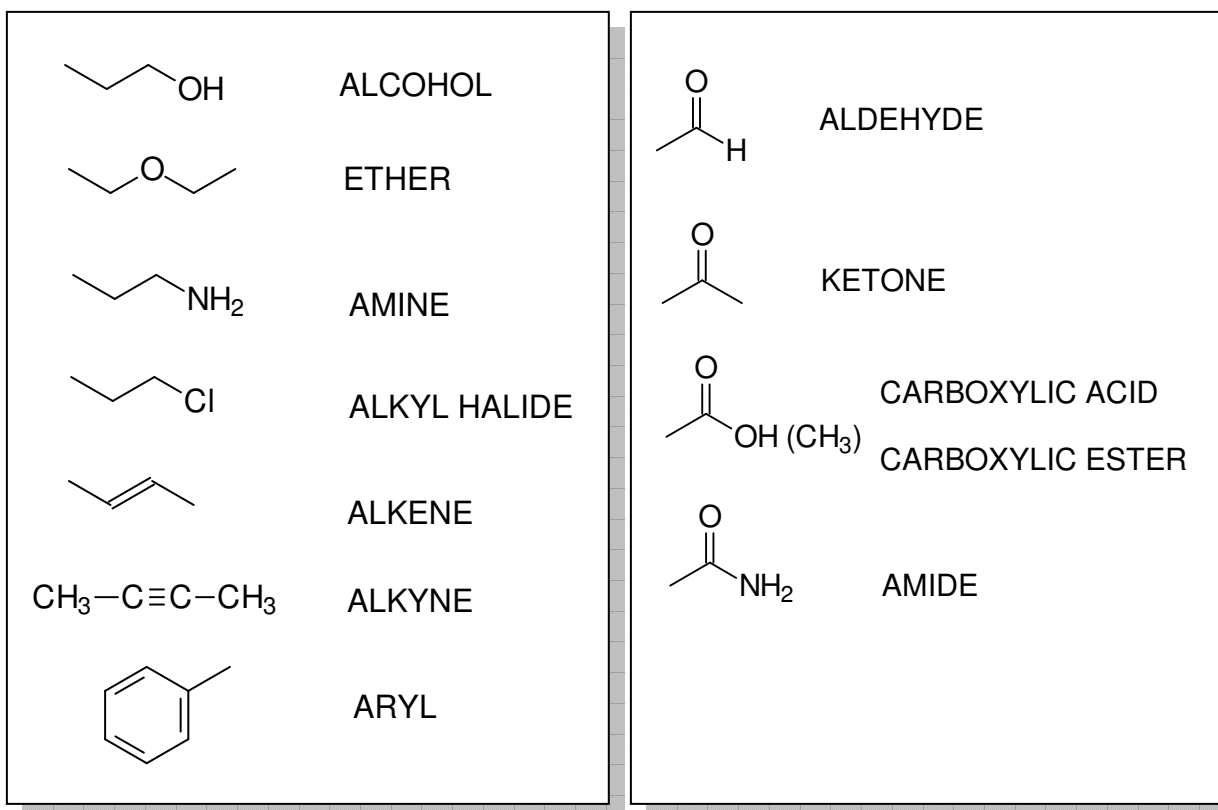


Figure 2: The most common functional groups found in organic compounds

There are lecturers who prefer to postpone any extension of this fundamental list of functionalities for a later time as the various chemical classes of compounds are introduced along the org chem courses. This is fine, but it misses a great opportunity to offer the first systematic approach to molecular buildup of components that make up the body of reactive organic molecules. This is not just a recognizing-naming game, but a first thorough introduction to what makes organic molecules so interesting and versatile.

This is what we intend to do now in the rest of this lecture.

## **SLIDE 6**

### **APPROACHING FUNCTIONAL GROUPS SYSTEMATICALLY**

There are many more functionalities any organic chemistry student and practitioner should be acquainted with. Trying to remember all of them as a shopping list (as many courses purport) is a perfectly useless proposal. We are going to use a little bit of systematics to approach this otherwise tedious subject, so remembering them will be much easier and instructive.

This is what we will do:

- 1.- Starting with a 'saturated' carbon we will add multiple bonds and...
  - 2.- Heteroatoms, chiefly O, N, S and halogens, either single bonded or with 'multiple' bonding.
- Simple enough.

The end result from a bird's eye is shown in fig 3:

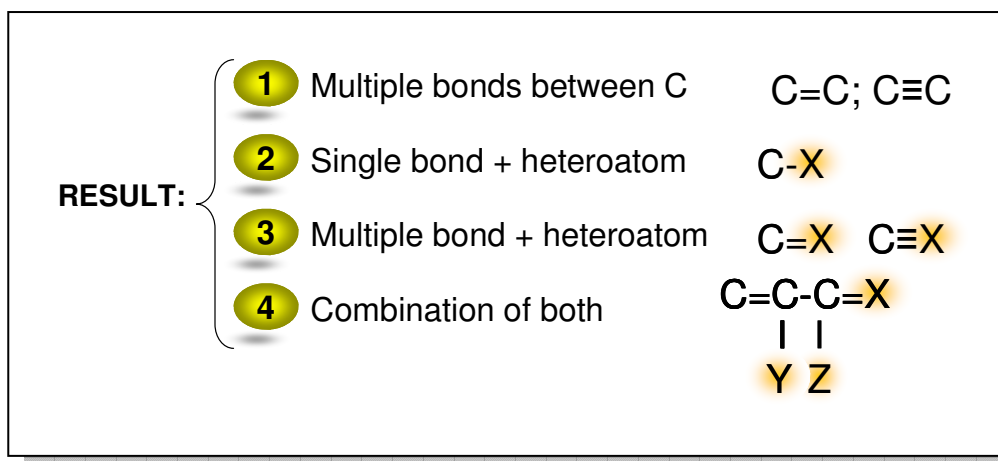


Figure 3: Sequence of adding multiple bonds to C with other C atoms and heteroatoms (X) as well that will be followed in building new carbon functionalities . Respective names will be given after their construction.

In fig 3. elements X,Y and Z earmarked in yellow design a heteroatom: halogen, N, O, or S.

By combining these simple elements and bonds it is possible to build almost all functional groups found in organics, common and not so common.

## **SLIDE 7**

### **SYSTEMATICS -2-: THE FUNDAMENTAL STRUCTURES AROUND CARBON**

The other trick we have to consider while building or recognizing functional groups is the bonding pattern around C using the fundamental bonds (single or multiple) of the previous slide.

All it takes is adding single and/or multiple bonds between the central C and other carbons, and/or other heteroatoms X.

In approximate order of increasing activity, this systematic addition of bonds leads to the progression of fig 4. What we come up with is a generic condensate of almost all functional groups found in organic compounds

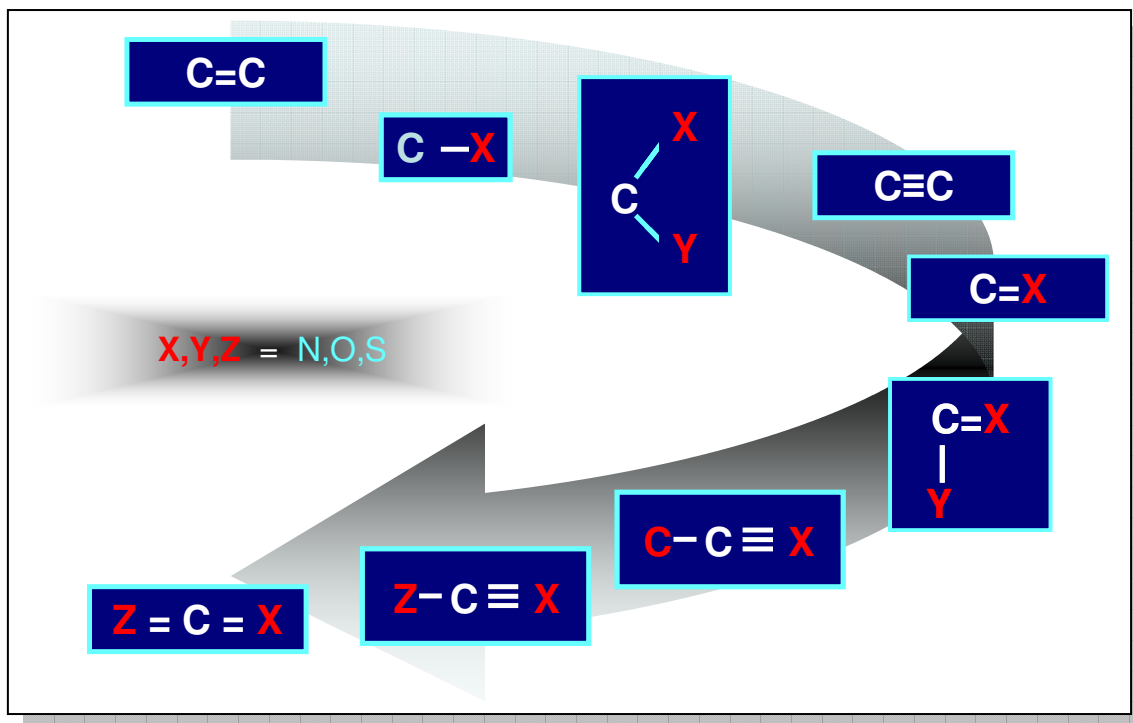


Figure 4: Result of adding progressively bonds and heteroatoms to a central carbon. From these simple combinations dozens of functional groups will emerge.

### **SLIDES 8-9**

#### **SYSTEMATICS -3-: A QUICK VIEW OF FUNCTIONAL GROUPS ASSOCIATED WITH EACH TYPE**

Each of these types leads to various functions. The following figures illustrate a number of functionalities that can be built from these simple partial structures:



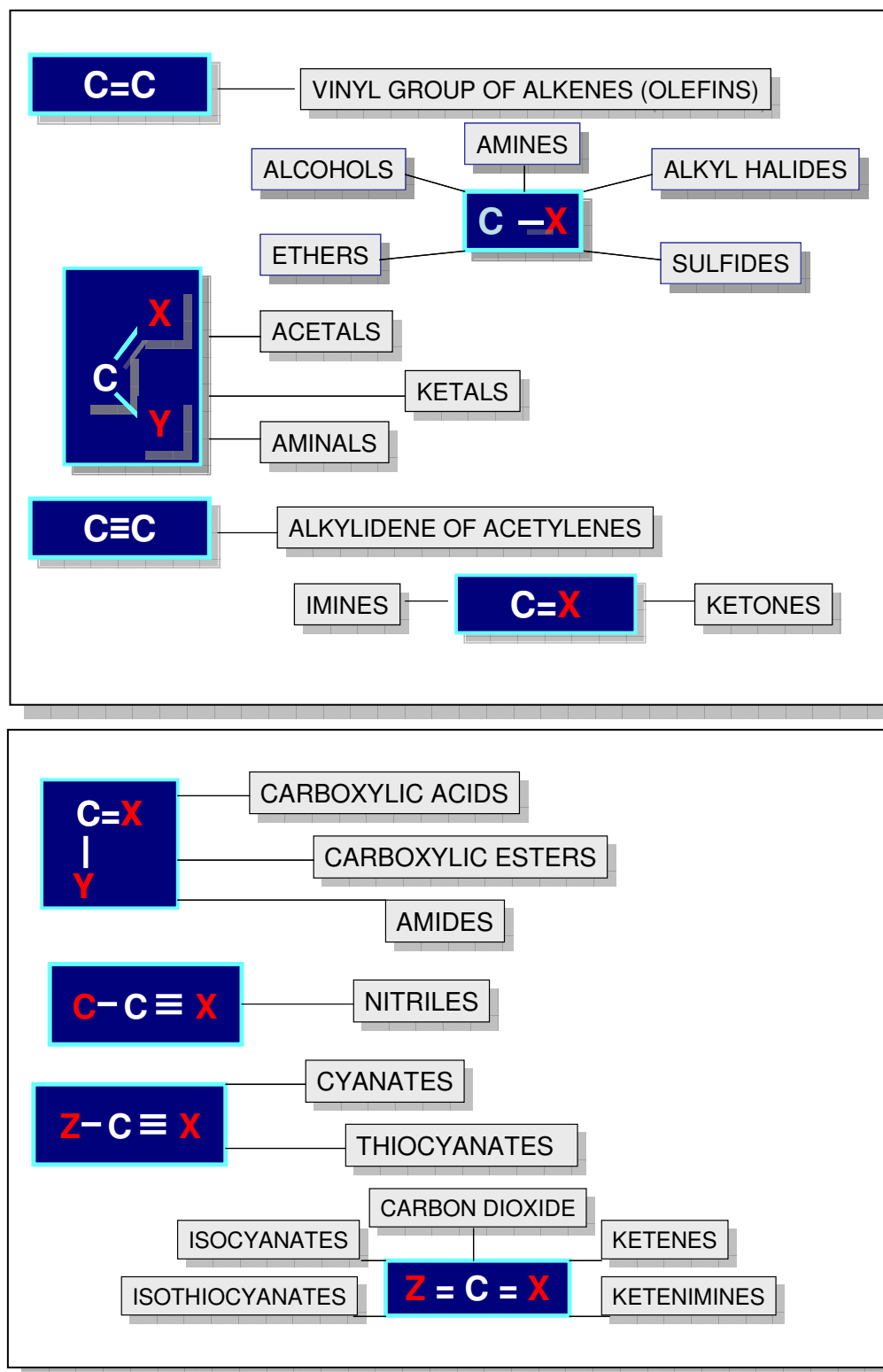


Figure 5A-B: An overview of functionalities derived from a few selected bond categories on C. Out of just 9 types, 23 functional groups are derived

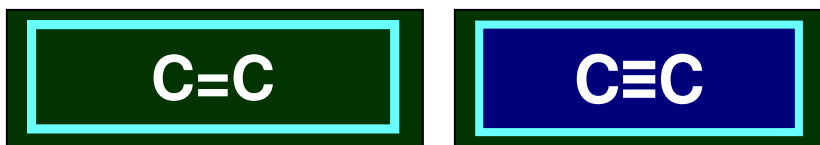
In the following few slides we will see in detail the specific functional groups of each kind evolving from the fundamental groups of atoms we just reviewed.

Unfortunately, it is important and unavoidable for the student to recognize right away *and memorize* structures of functionalities and their corresponding names. However, the systematic approach here undertaken will make this labor a lot easier and logical.

### **SLIDE 10**

STEP BY STEP -1-

FUNCTIONAL GROUPS BASED ON C=C AND C≡C



Based on the fundamental atom/bond combinations around C, we now proceed to develop a series of functional groups. We start with two C atoms with a double bond in the hydrocarbon series. For the moment no heteroatoms will be added.

Functionalities belonging to this group are generally at the *low end of the oxidation level*. Of course there are less oxidized compounds such as ethane and all the  $C_nH_{2n+2}$  hydrocarbons, but in these functional groups are absent.

This particular bond combination leads to five distinct functionalities which all the same have several properties in common (others differ):

As one can surmise from fig 6:

- 1) The C=C bond defines the VINYL group, also called ALKENYL, or ENE.
- 2) When the C=C unit is part of a alicyclic structure a cycloalkenyl group is defined, although it is very much the same as the open-chain function except for a few important properties of its own.
- 3) This C=C function comes isolated or in groups as in aromatics. Their 'conjugation' implies several interesting and unique properties.
- 4) A C≡C bond defines the alkynyl group as in acetylenes.
- 5) Two C=C bonds in tandem define the ALLENYL group, an eye-catching unit with peculiar structural and chemical properties.

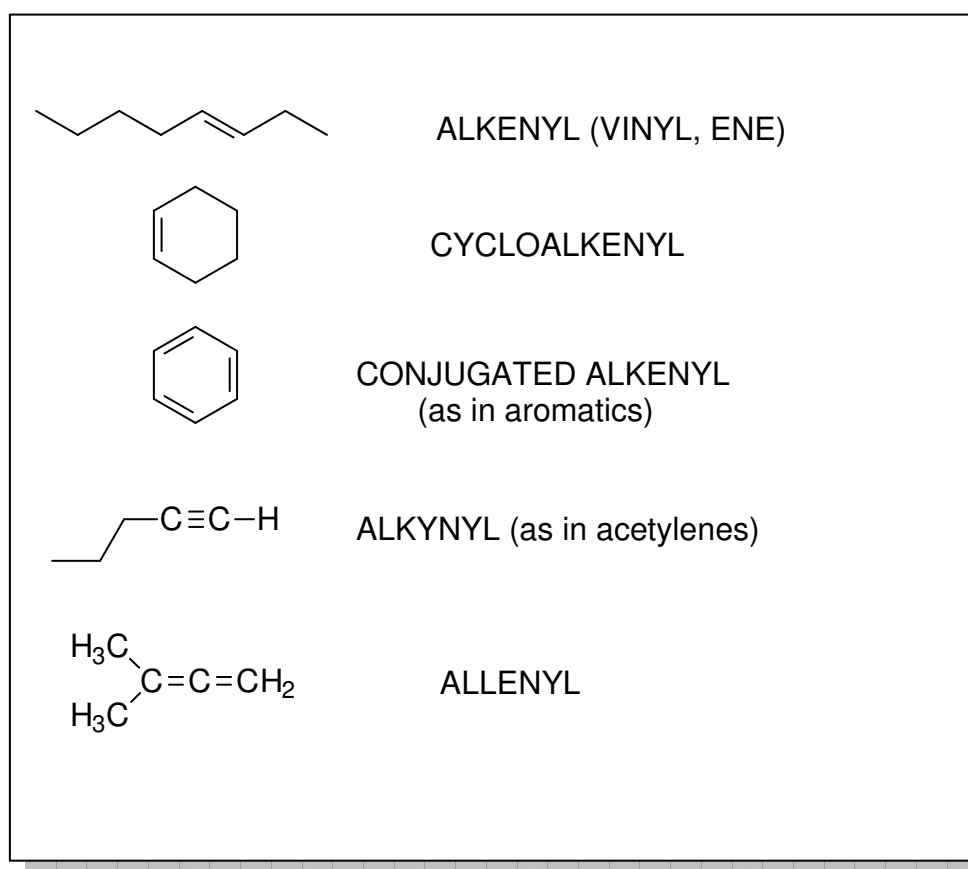


Figure 6: Examples of functional C based on the multiple bonding between carbon atoms.

**SLIDE 11****STEP BY STEP -2-****DEFINING FURTHER THE C=C GROUPS**

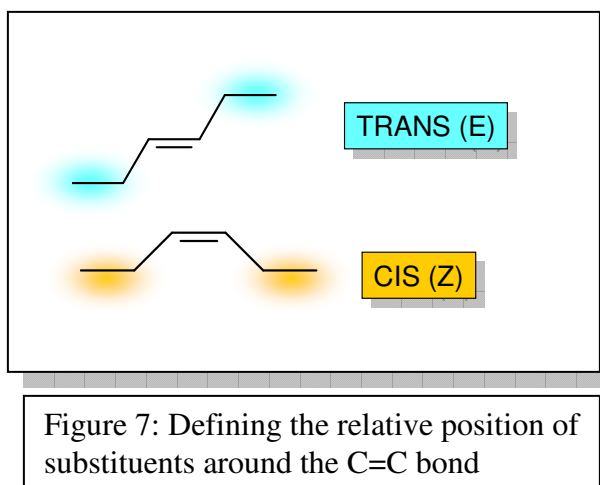
There are two issues to pay attention to when defining the alkenyl group.

- 1.- Relative position of substituents
- 2.- Naming C atoms in and around the C=C bond

In detail:

1.- The relative position of substituents

Owing to restrictions of the C=C bond to be seen in the chapter about alkenes (unable to rotate), those with two substituents on the ends (disubstituted alkenes).



This is equivalent to saying that the C=C bond lays in the C backbone, the substituents occupy positions on the same side or on opposite sides of the C=C bond. These are named *cis*, (or more appropriately *Z*), and *trans*, (or *E*), as shown on fig 7

2.- Carbons in and around the C=C also have specific names (fig 8).

The C atoms sharing the double bond are called **vinyl** carbons, while the vicinal CH<sub>2</sub> is named **allyl** carbons or methylenes.

Positions in and near the benzene ring have specific names: aryl and benzyl, as shown in fig 9

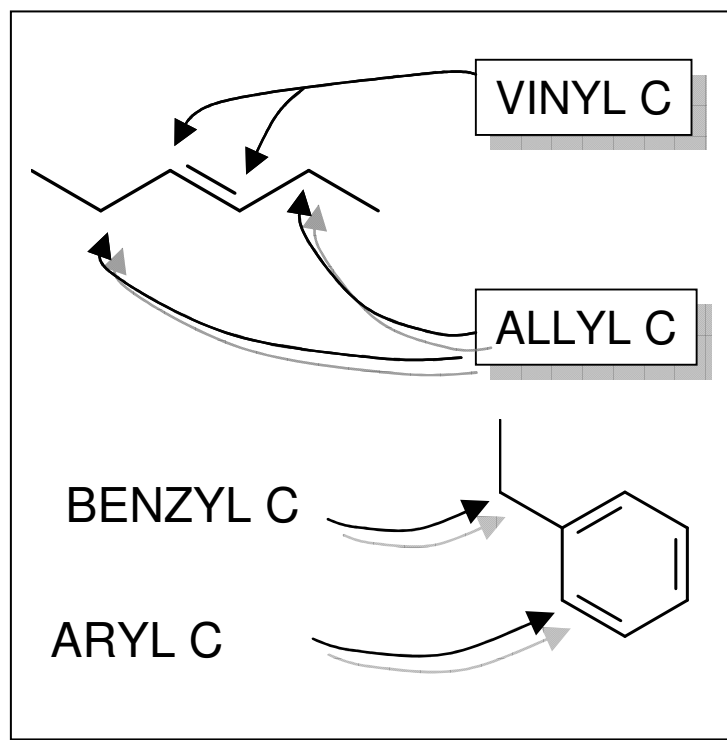
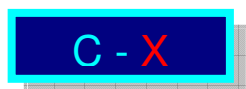


Figure 8: Defining unsaturated and vicinal carbons in vinyls and arenes

## **SLIDE 12**

STEP BY STEP -3-

FUNCTIONAL GROUPS BASED ON:



X = N, O, S, HALOGENS

X here is N, O, S and halogens. all commonly found in many organics, either natural or synthetic. This simple combination opens a whole host of possible functions.

Heteroatoms O, N, S and halogens may be single bonded to C giving rise to the functional groups shown in fig 9

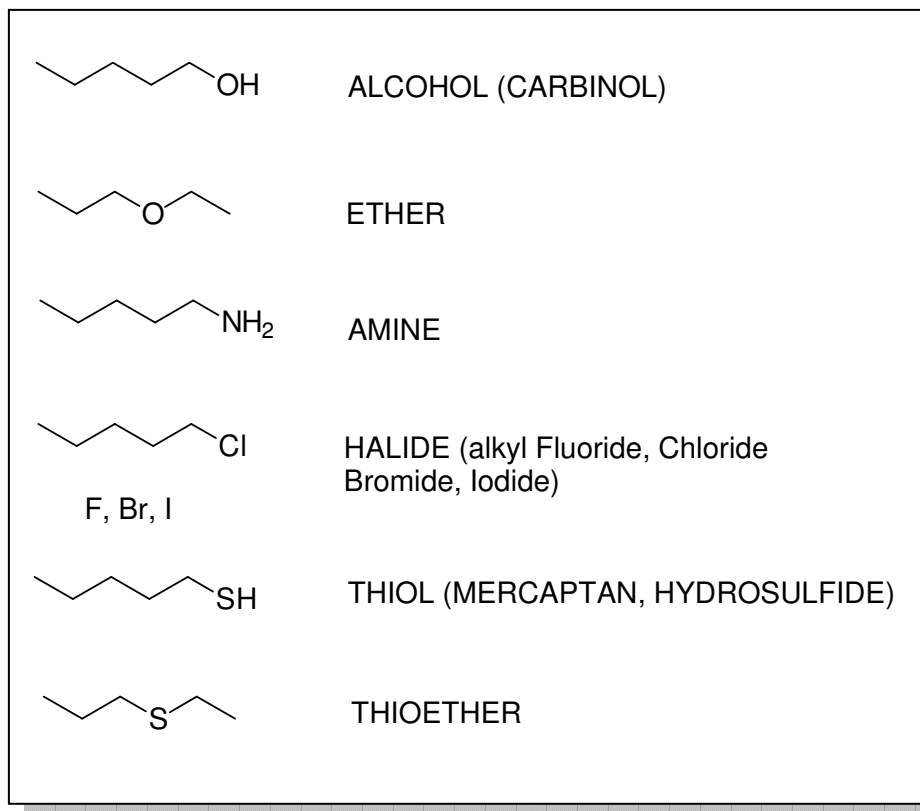


Figure 9: Representative examples of functionalities composed by a C-X bond (X = N, O, Halogens and S).

Alcohols (OH), amines (NH<sub>2</sub>), alkyl halides (X = F, Cl, Br, I) and thiols (SH) are created simply by forming a single (s) bond to saturated C.

On the other hand, inserting O or S in the carbon chain yields ethers and thioethers.

Doing the same with N gives rise to secondary amines (see later)

In the scale of **oxidation level**, these functions are placed in the next notch above the unsaturated hydrocarbons of the previous slides.

The shape and names of these groups are easily remembered, partly because they are commonly used and are part of the everyday language of science students. These compounds are found almost everywhere in daily life: food, pharmaceuticals, solvents, obnoxious compounds, perfumes...

### SLIDE 13

STEP BY STEP -4-

FUNCTIONAL GROUPS BASED ON:



Let's dwell for a while in the C-O combination. O is very common in organic functionalities. Why? The organic sphere of living organisms and materials lays at the bottom of a gaseous ocean –the atmosphere-loaded with 22% O<sub>2</sub>. a very reactive element which is easily incorporated in organics.

Oxygen, a divalent element, can therefore become associated with two atoms, H or C, and others, like in ethers for example. Moreover there might be more than one O atom in the same molecule giving rise to functionalities so common that they possess their own names.

In particular:

If the vicinal C is occupied by OH the unit is now a **glycol**, (have you ever heard about ethylene glycol in antifreeze coolants, and polyethylene glycol PEG?). Three OH's in a carbon chain will become a **glyceride**, whose parent compound is **glycerine**, Nitroglycerine is a naughty **derivative**

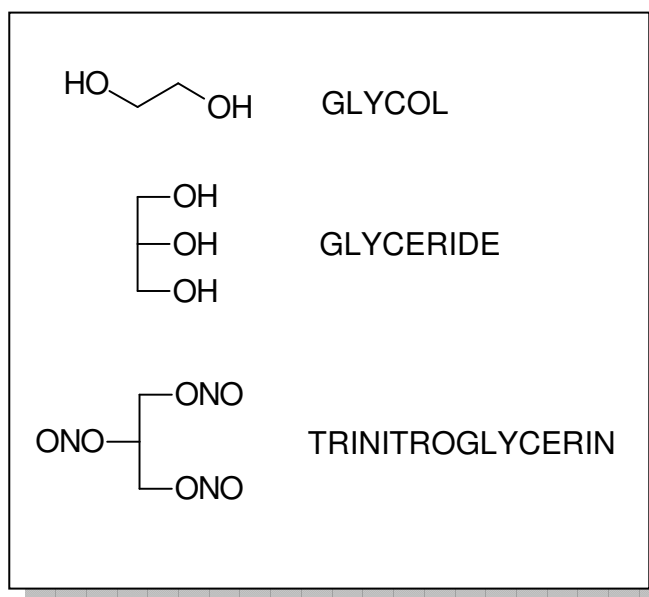


Figure 10: common carbon functional groups containing more than one OH unit.

Then there are the cyclic ethers: Figure 11 includes some examples of O embedded in cyclic compounds. Although they possess specific names, they belong to an ample class of alicyclics (cyclic compounds): the **heterocycles**.

Oxygen forming a three-member ring with C is an **epoxide**. This is the main functionality in epoxide resins and glues.

Oxetanes come from a 4-member ring, while the 5-member homolog is called **tetrahydrofuran**, whose parent compound is furan.

Larger rings such as the 6-membered one are named **pyran**, the fundamental structure of glucose (really a tetrahydropyran), a brilliant result of organic evolution, and its well known polymer: **cellulose**. Along with hemicellulose, this is the most abundant organic compound in the biosphere.



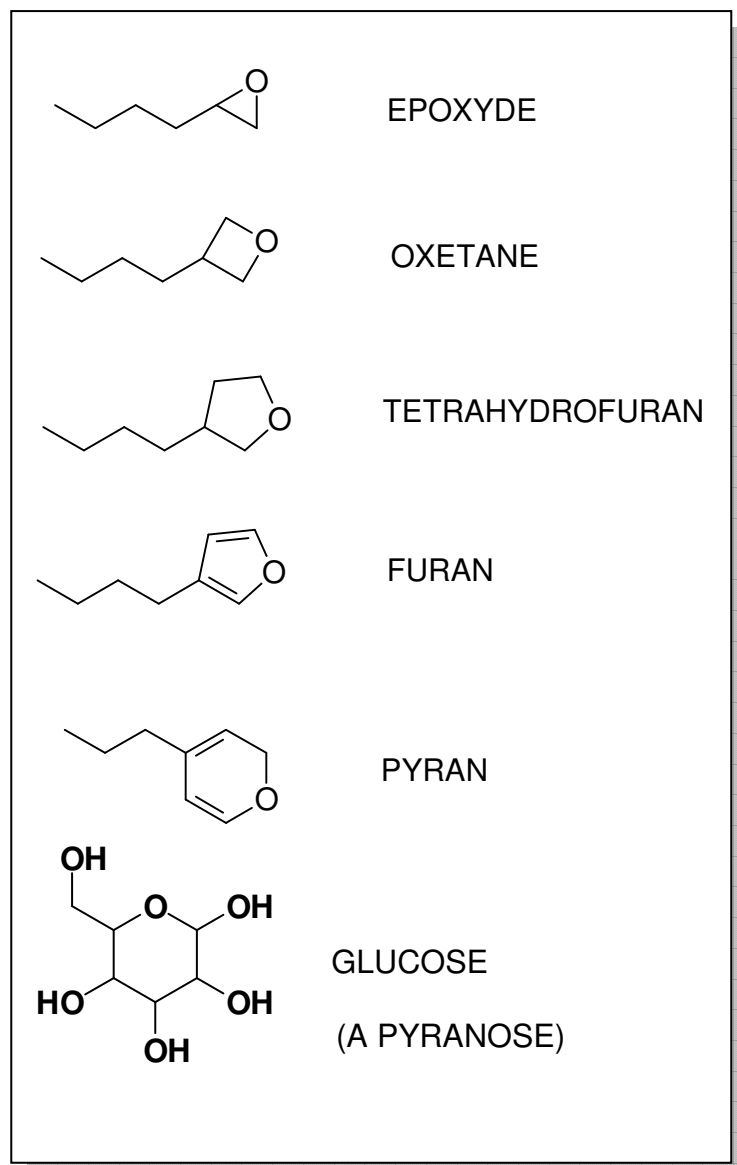


Figure 11: Examples of cyclic ethers

Similar organic functionalities may be constructed with N, S and combinations of O, N, and S. At this point we will not go into this for clarity sake.

**SLIDE 14**

STEP BY STEP -5-

FUNCTIONAL GROUPS BASED ON N AND S:

INSERTING MORE THAN ONE HETEROATOM IN THE CARBON CHAIN



This bond arrangement containing two heteroatoms in a row expands the structural versatility and reactivity of organic compounds (fig 12):

- 1) When X is O **peroxides** are formed. If the function occupies the end of the chain (as ROOH) the denomination turns to **hydroperoxide**. Extremely reactive and explosive, they furnish highly reactive O• radicals which intervene in various tissue degradation processes, aging, and cancer. However, some natural products with the RO-OR function are also useful therapeutic agents such as artemisinin, from Artemisia plants, against malaria.
- 2) When X is N **hydrazines** take shape. The parent compound H<sub>2</sub>NNH<sub>2</sub>(hydrazine) used to be a component of rocket fuel, although there are other industrial uses as well.
- 3) Inserting 2 and 3 sulfur atoms yields **disulfides** and **trisulfides**. Such sulfur bridges participate actively in protein structure. Some edibles such as onions, chives and garlic contain disulfides with healthy attributes.

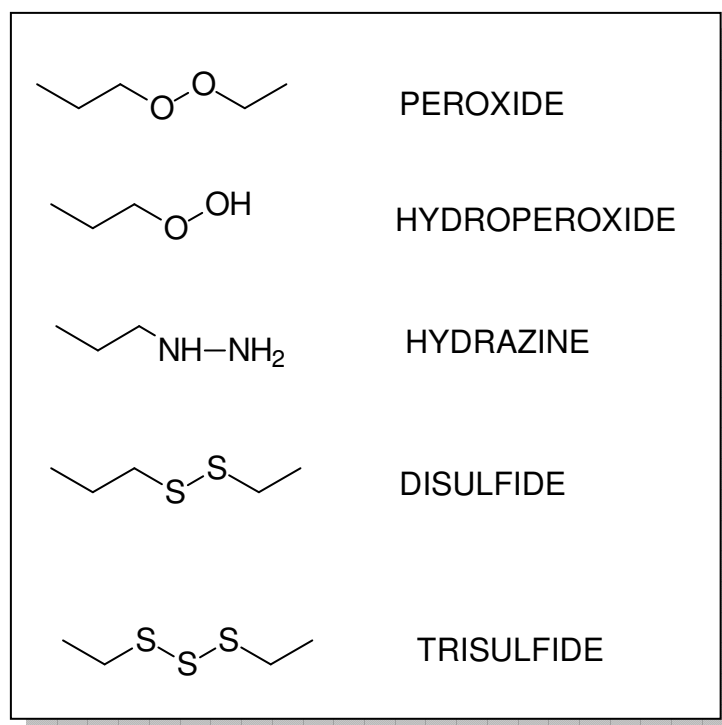


Figure 12: Functional groups containing two or more contiguous heteroatoms

### **SLIDE 15**

STEP BY STEP -6-

FUNCTIONAL GROUPS BASED ON N AND S  
AT A HIGHER OXIDATION LEVEL



This bond combination would be the homologs of the previous groups comprising peroxides, hydrazines etc.

The reaction possibilities of organics increases considerably as the functional groups become more diverse. This is achieved at a

higher oxidation level, e.g. adding more heteroatoms and/or multiple bonds to the element single bonded to C.

A first group is constructed from C and N of  $sp^2$  and  $sp$  hybridization (*see lecture on Valence bond theory*).

The simplest one in this group is the **nitroso** functionality sitting always at the extreme of a C chain (fig 13). This highly reactive function is associated with the development of certain types of cancer.

Adding a second O atom gives the **nitro** group, which induces considerable reactivity to the vicinal C. It is a common component of several explosives including nitroglycerine and trinitrotolulene or TNT.

The triple bonded  $N_2$  unit appears associated with C as a monovalent salt, thus receiving the denomination: **diazonium salt**. This function is commonly found in synthetic pigments and is an excellent tool in organic synthesis involving substitution reactions.

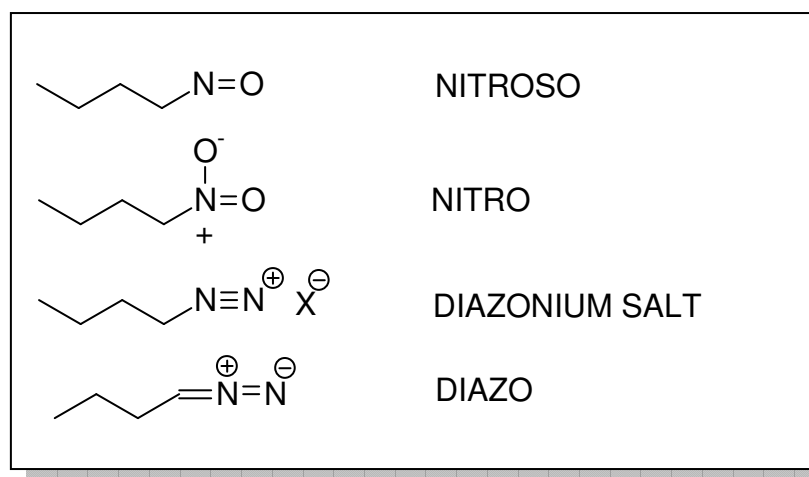


Figure 13: Common functional groups with N at a higher oxidation level.

Finally, the **diazo-** function, also composed of two N in tandem, is built with the rather curious electronic distribution of a zwitterion, or internal salt with positive and negative charges in the same molecule.

Sulfur shows a wider oxidation pattern allowing up to four O atoms owing to the expanded electron shell of 18 electrons. Note that the **R-C≡S** combination is **not allowed**. Of interest to organic chemistry one has (fig 14):

- 1) **Sulfoxides** by adding 1 O atom, such as in dimethyl sulfoxide, a common solvent.
- 2) **Sulfones** by adding 2 O atoms. These are useful intermediates in synthesis
- 3) **Sulfonic acids** by adding 3 O atoms. These are strong organic acids mimicking the role of sulfuric acid.

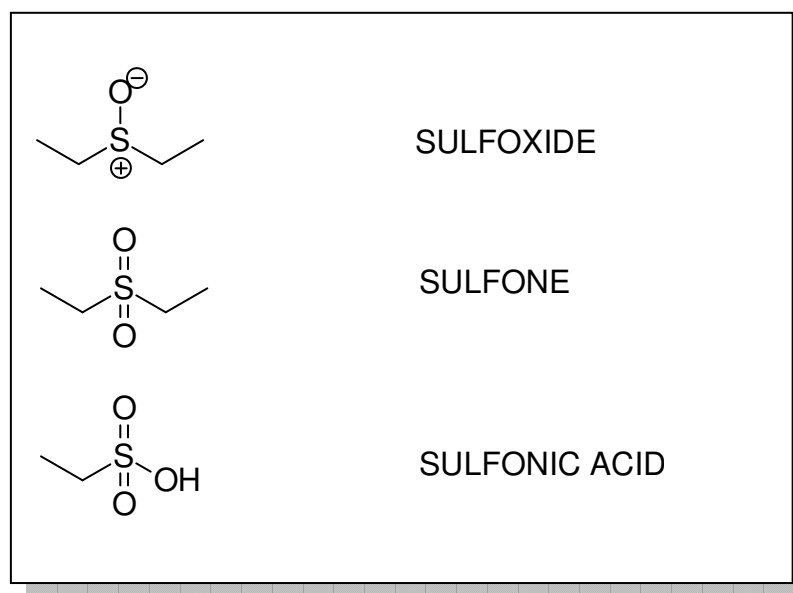
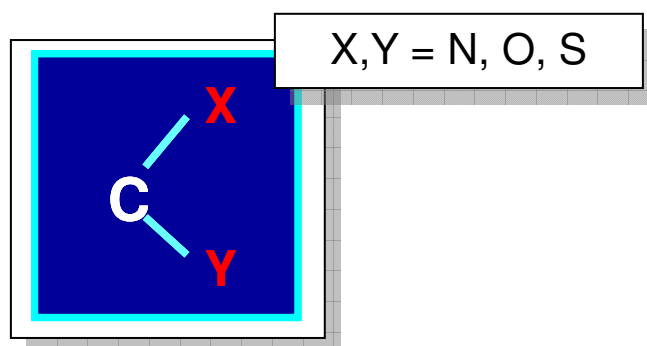


Figure 14: Functional groups containing S at higher oxidation levels.

**SLIDE 16**

STEP BY STEP -7-

ADDING TWO HETEROATOMS ON SATURATED C.



We have reviewed a number of cases with only one heteroatom but up to four valences of C may be occupied by heteroatoms. The next step up would be **two** heteroatoms as shown above.

Adding one more OH to the **carbinol carbon** gives **hydrates**, which are rather unstable units (fig 15) although some useful anesthetics such as chloral are used in veterinary medicine. These become much more stable if the O atoms are alkylated. These are known as **acetals** and **ketals** (fig 16). Acetals possess a CH unit between the pincers of the two heteroatoms (the anomeric proton), whereas in ketals this proton is absent.

These functions have been studied extensively as protective groups in organic synthesis and several cyclic derivatives exist. Many bioactive natural products contain the acetal function as well. If O is replaced with S, the functionality is named **thioacetal** and **thioacetal**, again with cyclic versions.

When N is used instead, an **aminal** is formed. A combination of N and O yields the **semiaminal**.

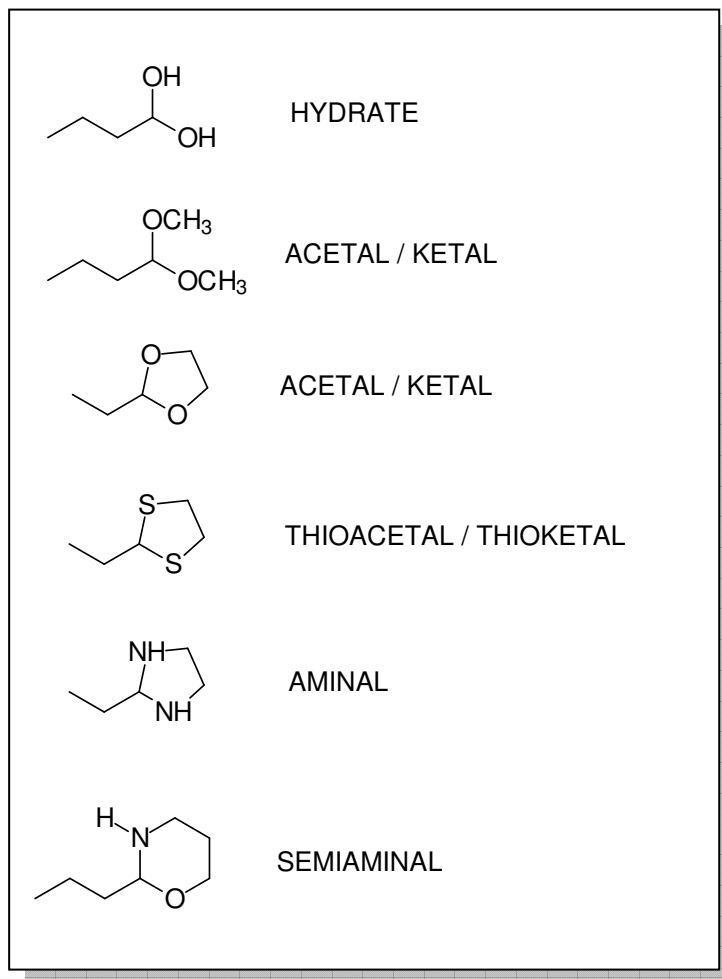


Figure 15: Common functional groups with two heteroatoms bonded to saturated carbon

## SLIDE 17

STEP BY STEP -8-

ONE HETEROATOM DOUBLE ( ) BONDED ON C



where  $X = N, O,$  or  $S$ .

Among these functions (fig 16) there is the  $C=O$  group, the most widely found functionality in organic compounds, natural or synthetic. Its formal name is **keto, carbonyl, or oxo**.

**Aldehydes** contain this carbonyl group always at the end of the carbon chain. In **ketones**, the  $C=O$  unit is bonded to two  $C$  atoms, and thus form an integral part of the carbon chain or cycle.

Replacing  $O$  by  $N$  gives **imines and oximes ( $C=N-OH$ )** while  $S$  gives **thioketones**.

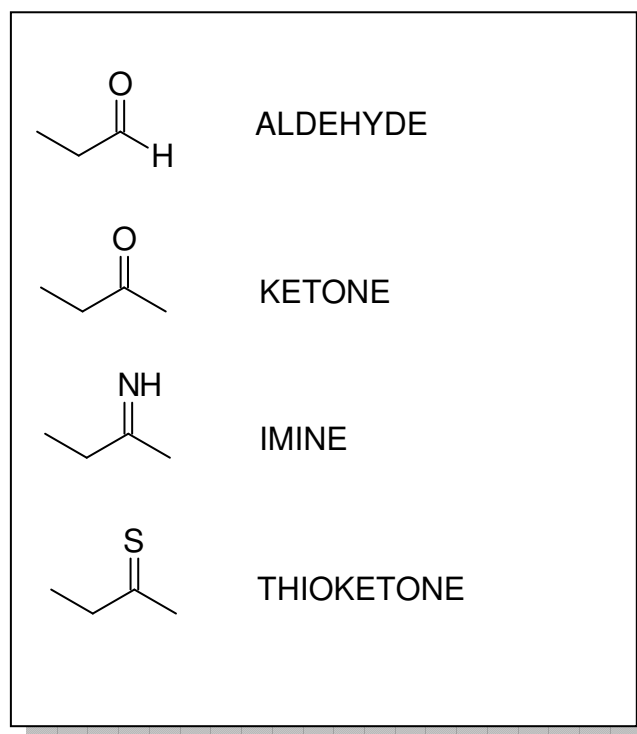


Figure 16: Functional groups including the  $C=X$  combination, among which are the well known aldehydes and ketones.

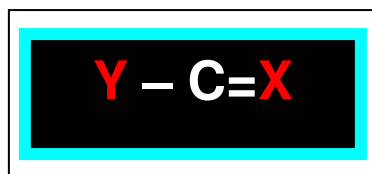


There are a number of chemical properties of compounds containing these functions, either spectroscopic, structural or reaction patterns that make these functionalities a very useful tool to have around for synthetic transformations.

### **SLIDE 18**

STEP BY STEP -9-

ONE HETEROATOM DOUBLE ( ) BONDED ON C PLUS ANOTHER SINGLE ( ) BONDED HETEROATOM



where X and Y are O, N, or S. At this level of the course, it will suffice to consider groups with X = O only (fig 17).

The most important and commonly found function is the **carboxylic acid**. In its deprotonated form it becomes a **carboxylate**.

If the proton is replaced with an alkyl group, say a methyl, the carboxylic acid is now an **ester**, or **carboxylic ester** more correctly.

Next in line are **amides** and **thioesters** in which the heteroatom at the end is N or S, respectively.

There is a special case of esters that adopt the cyclic form. These are named **lactones**. Four membered rings are **beta-lactones**, five membered: **gamma-lactones**, and six membered: **delta-lactones**

Cyclic amides are formed likewise. These are named **lactams**, using the same alpha, beta and gamma prefix depending on the ring size.

All these functions are reactive chiefly at the carbonyl carbon. The most reactive of all, however, is the acyl halide (chloride etc) function shown in fig 19. Water reacts with a lot of heat being produced, an indication of a favorable and fast reaction taking place.

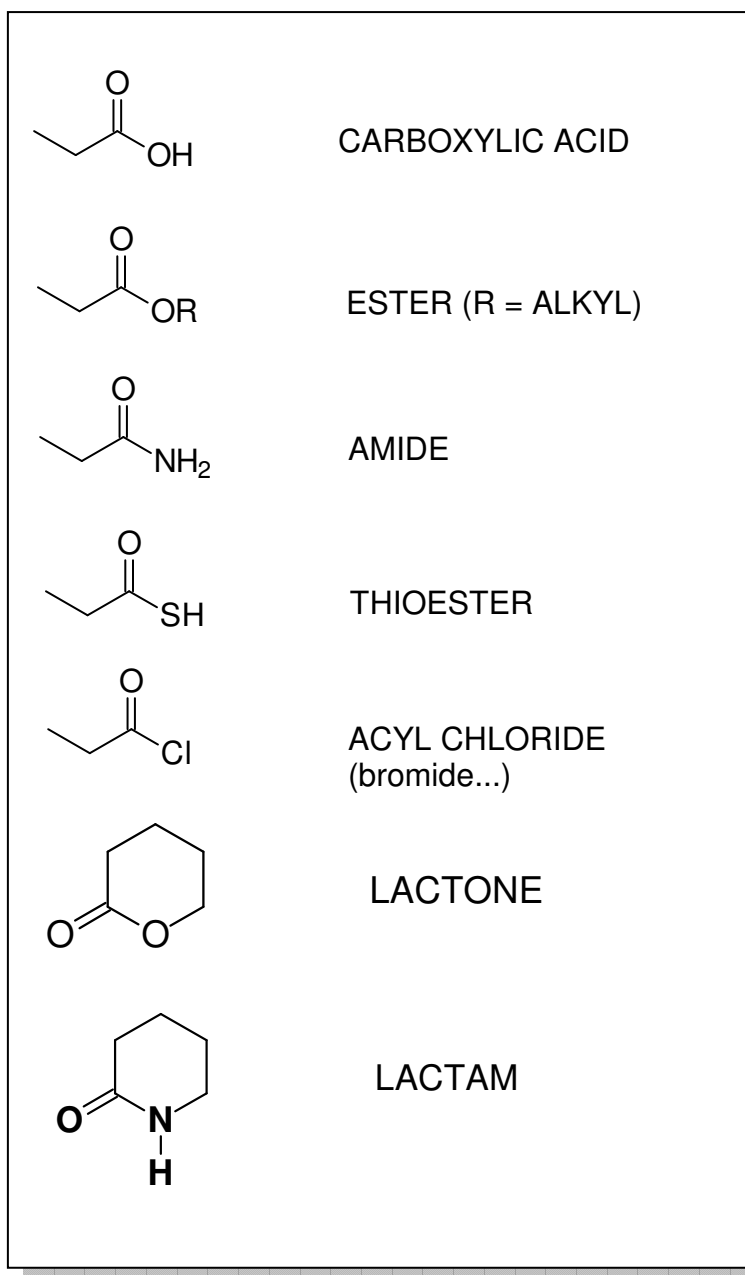
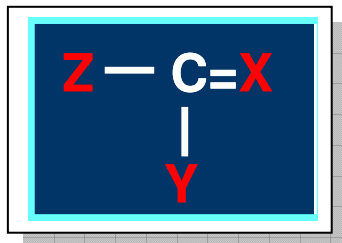


Figure 17: Aliphatic and alicyclic derivatives of the fundamental carboxylate function

**SLIDE 19****STEP BY STEP -10-  
ADDING THREE HETEROATOMS**

Where X, Y and Z = N, O, S

This is a versatile arrangement furnishing a number of functional group types. These functionalities are generally less commonly found though, but are still important (fig 18).

**Carbonate esters** contain three O atoms in the functional group and are found in some important natural products.

Replacing one O with N at the end gives a **Carbamate**, which one finds in third generation insecticides and other bioactive materials.

Alkyl **ureas** replace two O atoms whereas replacing all of them with N gives the all important **guanidines**, compounds of great biochemical relevance.

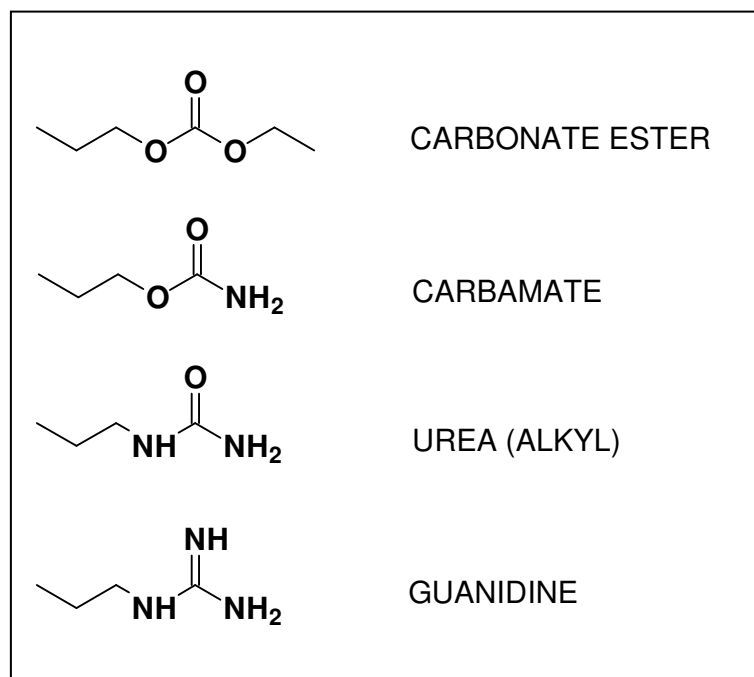


Figure 18: Highly reactive functional groups containing three heteroatoms on an unsaturated carbon atom.

## SLIDE 20

STEP BY STEP -11 -

ADDING TWO HETEROATOMS MULTIPLE BONDED TO C

The model now has two different arrangements:

A:



B:



There are several highly active functions included in these two structural types of functionalities (fig 19). Except for nitriles, ketenes and allenes, most of them are not encountered in elementary courses of organic chemistry. However, some acquaintance with them will aid in chapters dealing with addition reactions is mandatory as many industrial products utilize these functionalities.

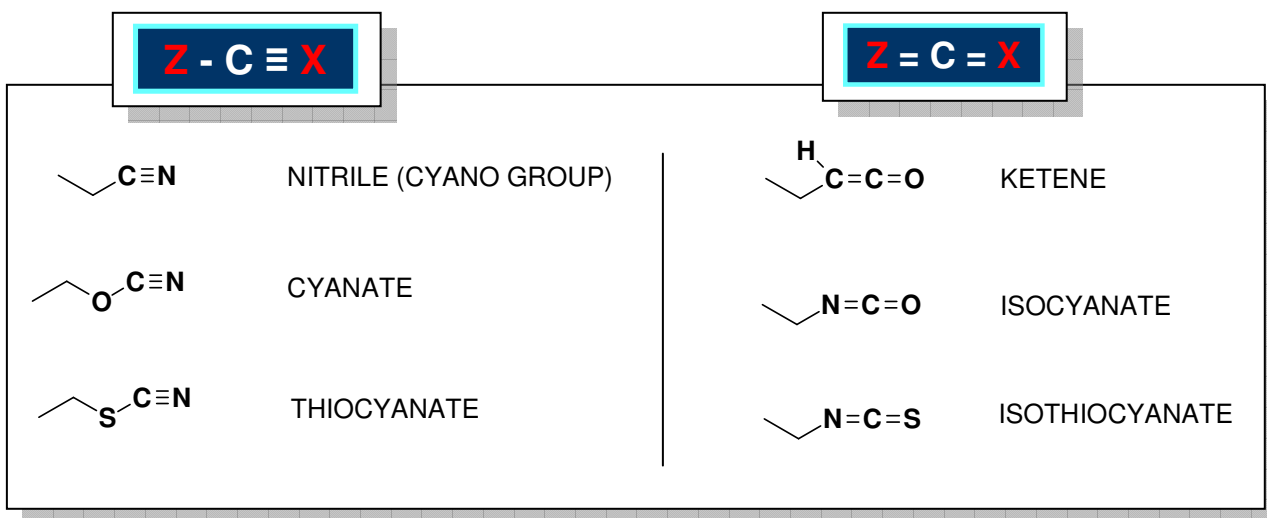


Figure 19: Functional groups including a disubstituted central carbon. Z stands for C, N, O and S; X for N, O, S

## SLIDE 21

### PUTTING IT ALL TOGETHER

This slide is an overview of all structural types and their most common functional groups. It is good training for students to associate structural type and functionality, as this involves useful definitions when other more advanced chapters are studied.

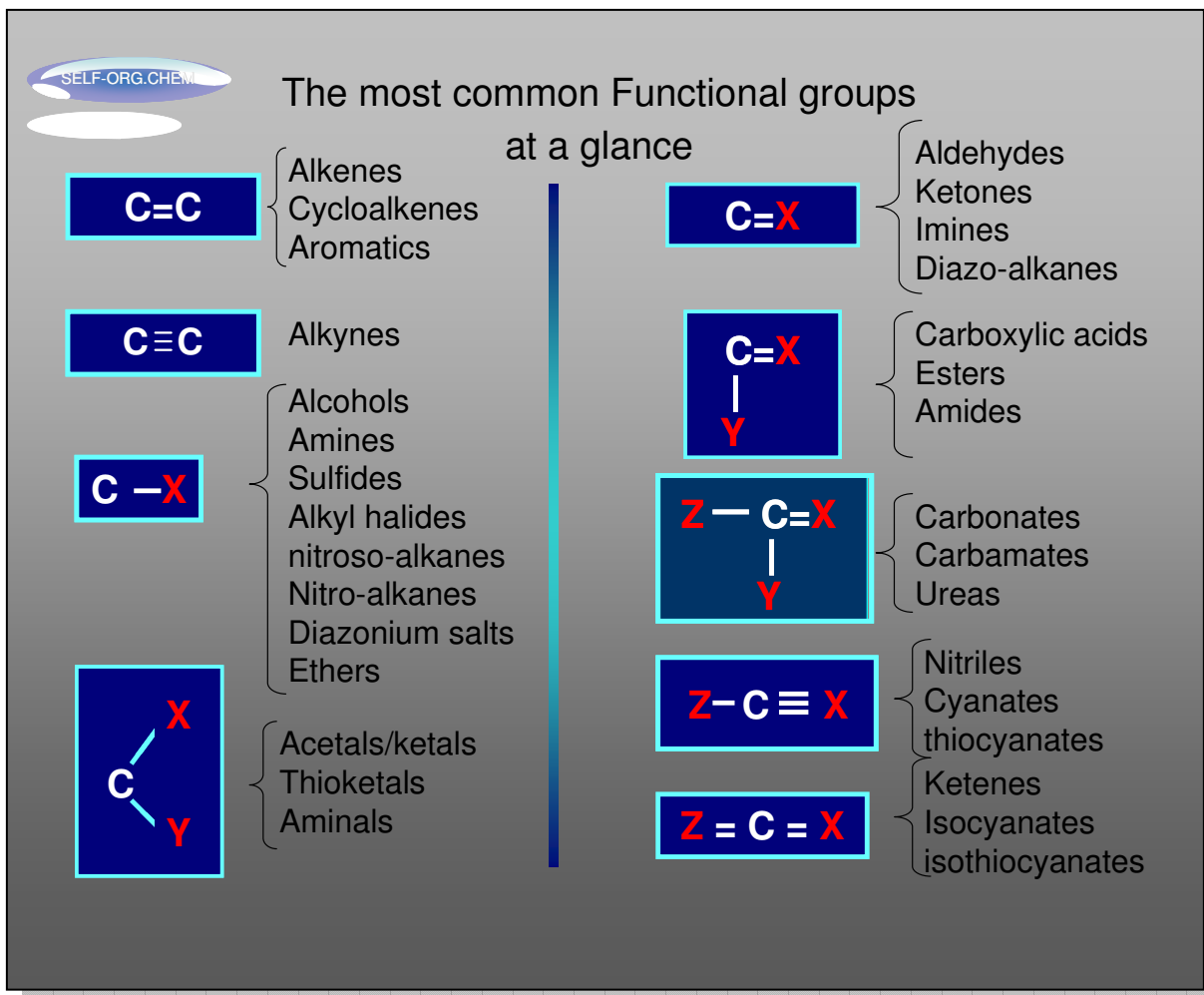


Figure 20: Overview of substitution patterns in C and names of common functional groups belonging to each pattern.

### CONCLUDING REMARKS:

(no slide)

Functional groups are what make organic molecules chemically interesting. Carbon atoms build around themselves wonderful molecular skeletons, as those found in fossil fuels

However, these carbon skeletons are reluctant to react unless subjected to high temperature and/or catalysts and in the presence of

highly reactive species. The insertion of multiple bonding between C atoms and also heteroatoms of the second and third row of the periodic table increases tremendously the reactivity pattern and lowers the activation energy required for chemical transformations.

Obviously, the C-X, C=C and C=X bonds influence life and function of organic molecules profoundly. Their association in sets of atoms/bonds named functional groups makes this possible. Reasons for this remain deep in the atomic composition and elementary properties, which will be reviewed in detail in a later lesson (see lectures on Bonding in Organic compounds, of this Self – Org - Chem series).



ADDITIONAL MATERIALS INCLUDED IN THIS PACKAGE:

PROBLEM SHEET

PRINTABLE LIST OF  
FUNCTIONAL GROUPS

## HOW TO USE THIS MATERIAL

The instructional materials of this lecture are:

- 1) This script
- 2) A set of interactive slides with advanced graphic features in Microsoft PowerPoint®
- 3) Action buttons for slide control
- 4) Embedded quizzes
- 5) A problem sheet

### SCRIPT

This scrip is just a suggested guide intended to help you in the sequence of arguments of each slide, not a rigorous script to be followed word by word. Lecturer should provide his/her own personal language, ideas, examples, style and so forth based on these suggestions, of course.

The script may contain also information on the side: old short stories from the history of organic chemistry, curiosities, relevance of some compounds in industry and biology etc.

The script may be used as class complementary material for students by uploading it in a local network. It is designed as an organic chemistry text with illustrations, reaction schemes and many of the visuals shown in the slide show.

*This scrip is just a suggested guide to help in the sequence of arguments of each slide, not a rigorous script to be followed word by word. Lecturer will provide his/her own language, ideas, examples, and so forth base on these suggestions. Move forward images by clicking on mouse, but wait for animations to finish first for best impact*

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### SLIDE SHOW

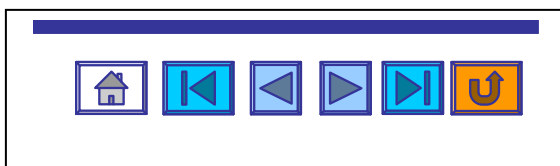
Slide numbers indicated in subtitles are those shown on the upper right corner of the actual slide. Generally they are TWO numbers BEHIND the actual slides in the PowerPoint sequence. Slide 1 is used for the mandatory copyrights page, lecture title appears on slide 2, and, slide 3 is for the lecture contents. The latter will be Slide 1.

Move forward images by left-clicking on mouse or using the arrows on the keyboard, but wait for animations to finish first for best visual impact and educational effect. Presentation of text, molecular renderings, equations and images have been designed and timed carefully to be shown with argument progress and not in overwhelming shots of data as in many slideshows. To take advantage of these highly educative effects, I strongly recommend lecturers to please become acquainted first with these visuals before class and control commands of each slide before presenting these lessons so they are in control of animations along their discussion

The flag marking the end of the last animation in each slide is a HEXAGON framing the slide number on the upper right corner, also showing the slide number.

### ACTION BUTTONS

In various places along the slide show there are action buttons to travel to selected slides. Wiggle a little your mouse to activate the pointer and drive it to the selection button. The customary little ‘hand’ will appear, click on your selection and travel to that slide to jump back and forth as you wish.



At the lower right corner, almost all slides display a set of action buttons. These buttons allow you to move forward and backwards to: Content slide (menu), previous, next, first and last slides, or quit lesson altogether.

### PROBLEM SHEET

There are many good sources available for study problems, to be sure. We have added a set of such problems that reinforce the particular subjects treated in this lecture.

Remember: Studying and using this material in class takes much less time than preparing the lesson from scratch, least of all using chalk and board or even web downloadable “fixed” and boring sets of cheap looking slides.

