Lecture

Review of Organic Chemistry and Herbicide Chemistry

1. Basic herbicide chemistry

- most herbicides are organic compounds, i.e. they contain carbon
- the major elements contained in organic herbicides in order of decreasing occurrence are carbon, hydrogen, oxygen, nitrogen, chlorine, phosphorus, sulfur, and fluorine
- the basic structural components of most organic herbicides are carbon chains (aliphatic groups) and rings (aromatic groups)

2. Chemistry and nomenclature of simple aliphatic compounds

- the simplest aliphatic compound consists of one carbon and four hydrogens (CH_4) and is a gas named methane
- a two carbon aliphatic compound is called ethane (C_2H_6); three carbons, propane; four carbons, butane, etc
- see Figure 5.1 (Chemistry and nomenclature of simple aliphatic compounds; page 6)
- when the radicals of these compounds are included as a portion of a large molecule they are similarly named but with -yl as the ending, e.g. methyl, ethyl, propyl, butyl, etc.
- an aliphatic group with a carboxyl group (- COOH) at the end of the chain is called a carboxylic acid
- a carbon chain in which one or more of the hydrogens is replaced by a hydroxyl group (- OH) is called an alcohol
- a carboxylic acid with two carbons in the chain is called ethanoic acid (or acetic acid); the two carbon alcohol chain is called ethanol (ethyl alcohol)
- see Figure 5.1 (Chemistry and nomenclature of simple aliphatic compounds; page 6)

3. Chemistry and nomenclature of simple aromatic compounds

- ring compounds or aromatics are derivatives of benzene (C_6H_6)
- a benzene ring minus a hydrogen is termed a phenyl group and in this form can accept an appropriate substitution
- a replacement of the hydrogen atom with a hydroxyl (- OH) group results in the formation of phenol
- see Figure 7.2 (Chemistry and nomenclature of simple aromatic compounds; page 7)
- substitutions can include benzoic acid, toluene, and aniline
- the positions on the benzene ring are numbered from 1 to 6 and also may be named
- positions 2 and 6 are the ortho positions; 3 and 5, the meta positions; and 4, the para position
- derivatives of organic compounds are named according to the functional groups and substitutions present
- see Figure 5.4 (Examples of how chemical terminology is used; page 8)

4. How chemistry affects herbicidal properties

- the chemistry of a compound determines how the herbicide will act in biological and physical systems such as plants, animals, soils, and water
- compounds made up of simple chains of carbon, hydrogen, nitrogen, sulfur, and oxygen tend to be degraded readily by microbes e.g. Roundup (glyphosate), Liberty/Ignite/Finale (glufosinate), and several thiocarbamate herbicides
- compounds with aromatic structures and halogen (chlorine, bromine, fluorine,iodine) substitutions tend to be longer lived than straight chains, e.g chloroacetamide, triazine, sulfonylurea, dinitroaniline herbicides
- the more chlorinated a compound the longer it will persist in soil
- the substitutions and alterations that can be made to an organic acid illustrate the effects that chemical structure can have on important herbicidal and mixing properties

<u>example of 2,4-D</u>
the acid form of 2,4-D is only slightly soluble in water and oil so use is limited in commercial formulations

<u>the acid can be reacted with bases to form salts</u>:
common salt formulations include sodium, potassium, ammonium, lithium, and several amine salts

these compounds ionize (dissociate) in water to form charged particles (see Figure 5.5; Major forms of 2,4-D; page 9)

all salts listed above are soluble in water with the amine salt being the most soluble and the most commonly used

salts are not soluble in oil and when used as foliar treatments must be applied with wetting agents to enhance penetration into the leaf

<u>the acid can be reacted with alcohols to form esters</u>:

esters of 2,4-D are nonpolar molecules and do not ionize (see Figure 5.5; page 9)

they are insoluble in water, but highly soluble in oil

during formulation they are usually diluted in oil-based solvents and mixed with an emulsifying agent (keeps the oil-ester droplets suspended in water)

oils may be used directly as carriers for application of esters particularly for treatment of woody species

✓ester formulations more readily wet and penetrate plant cuticles and are more toxic to plants than the salt formulations

✓the salts of phenoxy herbicides are non-volatile, whereas the ester formulations vary in their degree of volatility

volatility of an ester is determined by molecular weight of the alcohol:

short-chain, low-molecular-weight alcohols of five or fewer carbons lead to the formation of highly volatile esters

low volatile esters are heavier and consist of long-chained alcohols with an ether linkage (although called low volatile, they are still somewhat volatile) see Figure 5.5; page **9**

- effect of hard water on herbicide chemistry

hard water (water having high calcium or magnesium content; calcium content of 125 ppm) can affect herbicide stability

example of 2,4-D:

2,4-D dissociates in water, the sodium and potassium molecules are released leaving the 2,4-D anion

calcium and magnesium bind to the 2,4-D anion causing formation of precipitates that clog filters and nozzles

amine salts are less susceptible than the alkali salts to forming precipitates; the esters have excellent stability in water

example of Roundup (glyphosate):

in hard water, the isopropyl amine salt of glyphosate (see Lecture – Inhibition of Amino Acid Synthesis) reacts with $CaCO_2$ to form a calcium salt of glyphosate, which is not acceptable to the plant (does not readily pass through the cell membrane) resulting in decreased activity

to remedy the situation, ammonium sulfate (NH_4SO_4) is added to the spray solution.

the reaction of NH_4SO_4 with the $CaCO_2$ forms $CaSO_4$ and the ammonium salt of glyphosate this removes Ca as a factor affecting glyphosate activity

The ammonium salt of glyphosate is acceptable to the plant (readily passes through the cell membrane) and weeds are controlled.

- effect of water pH on herbicide chemistry

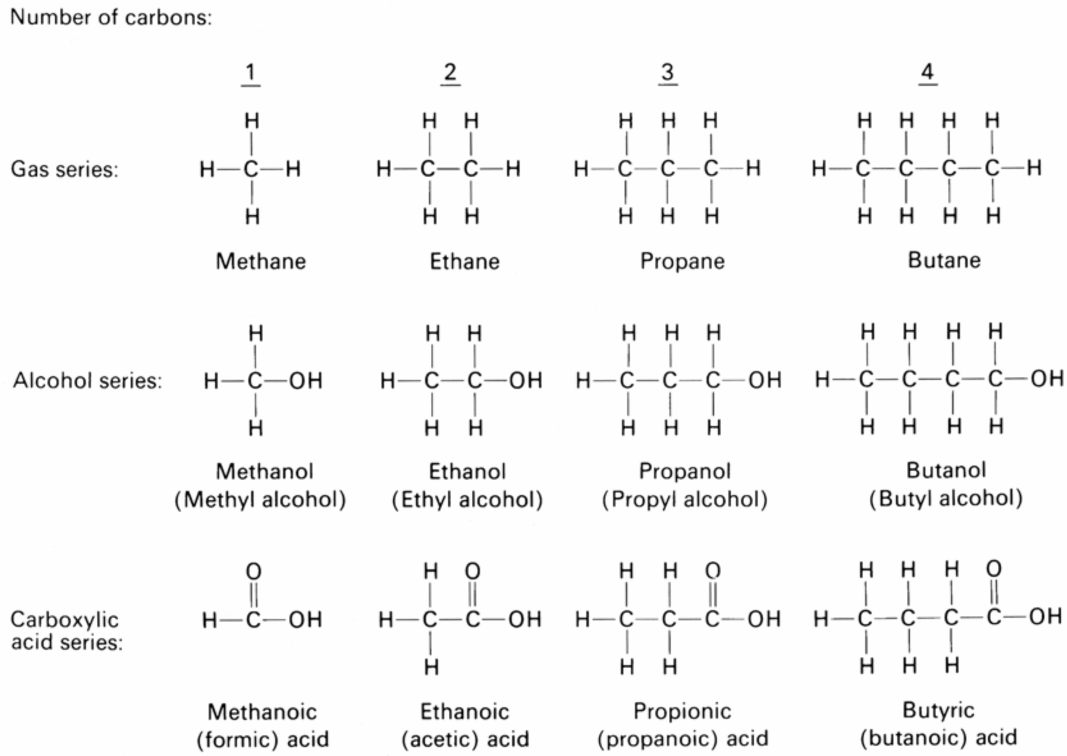
example of Asulox/Asulam (asulam):

High pH of water used as a herbicide carrier (pH of 8 or more) can result in the breakdown (degradation) of some herbicides through alkaline hydrolysis. This has been documented for Asulox/Asulam, which is used extensively for johnsongrass control in sugarcane.

To alleviate this problem, a buffer is added to the spray solution, lowering the pH of the spray solution.

5. Herbicide classification by chemistry

- most herbicides are classified into groups (chemical families) according to common chemistry
- chemical groups will have a common base structure and substitutions on the base molecular structure will determine the specific herbicide
- much of the remaining course will concentrate on herbicides classified by both chemical family and mode of action



Number of carbons	Compound	Radical
1	Methane	Methyl
2	Ethane	Ethyl
3	Propane	Propyl
4	Butane	Butyl
5	Pentane	Pentyl (amyl)
6	Hexane	Hexyl
7	Heptane	Heptyl
8	Octane	Octyl

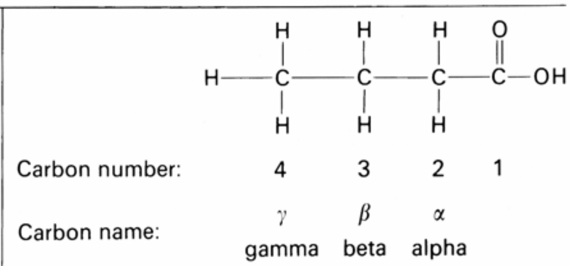


Figure 5.1 **Chemistry and nomenclature of simple aliphatic compounds.**

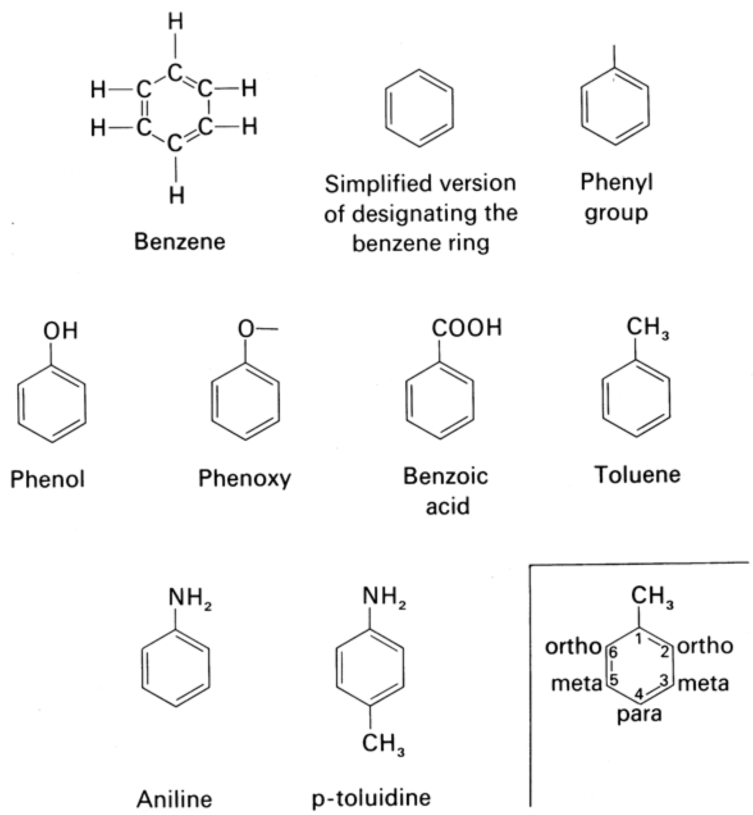


Figure 7.2. Chemistry and nomenclature of simple aromatic compounds.

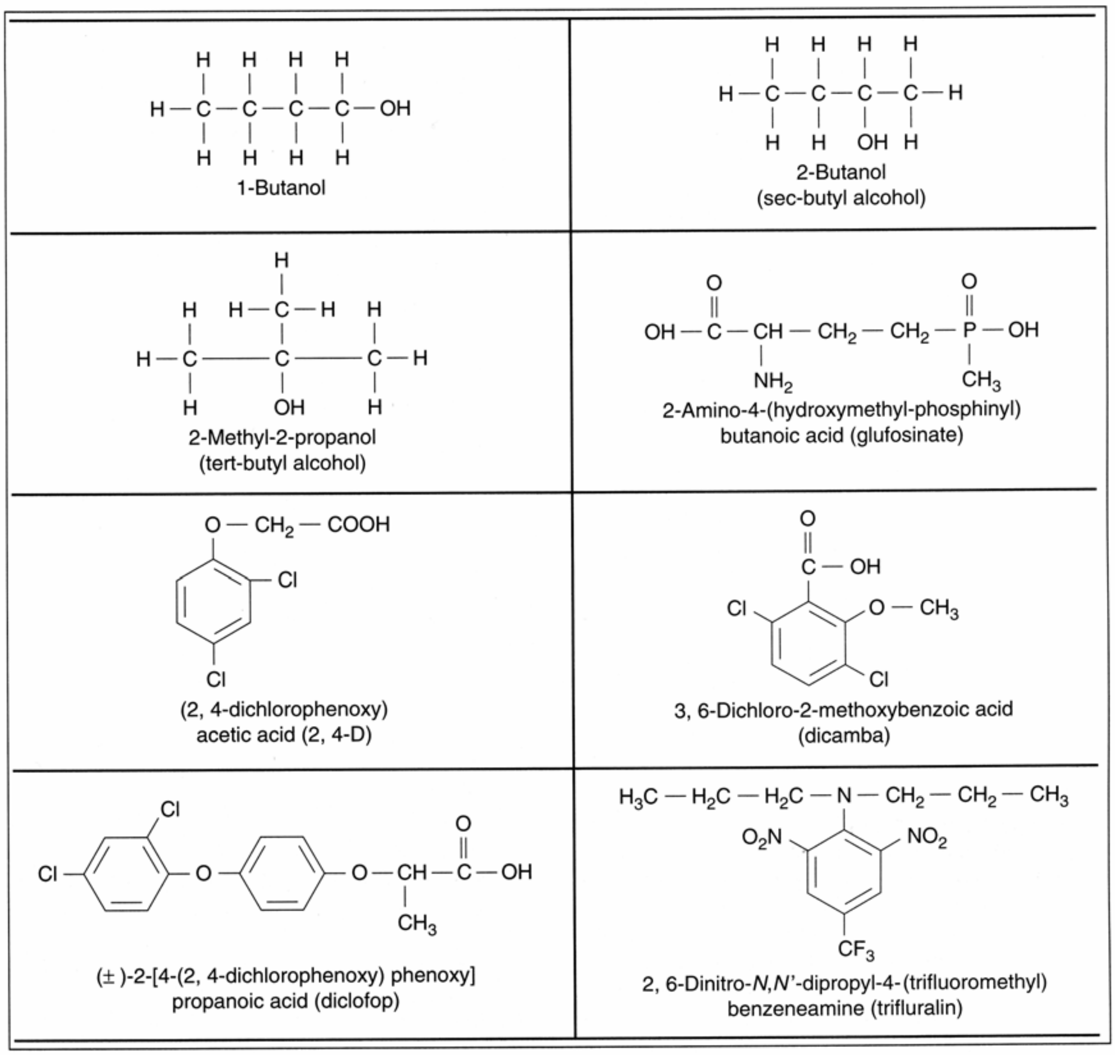


Figure 5.4 **Examples of how chemical terminology is used.**

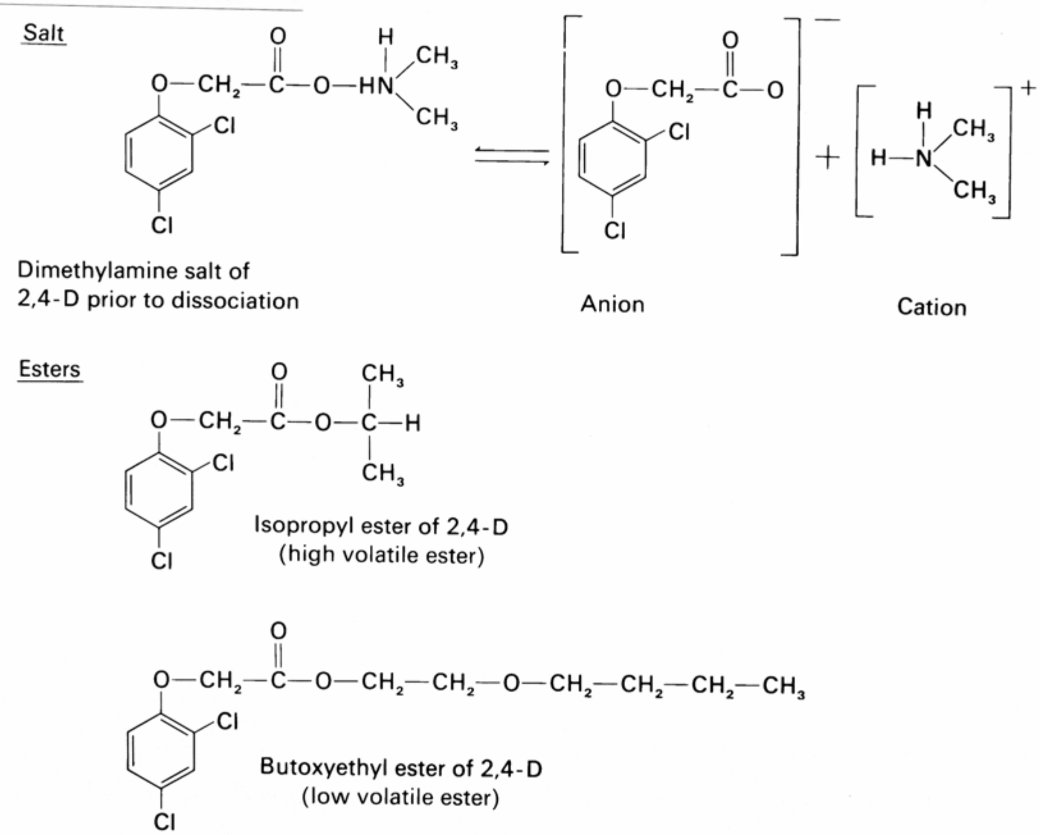


Figure 5.5 Major forms of 2,4-D.