COURSE CODE: *CHM 320*
COURSE TITLE: *Pesticide Chemistry*
NUMBER OF UNITS: *2 Units*
COURSE DURATION: *Two hours per week*

COURSE DETAILS:

Course Coordinator: **Dr. Lasisi, A. A. (B Sc., M. Sc., Ph D)**
E-mail: **lasialiyu@yahoo.com**
Office Location: **ROOM B 108, COLNAS**
Other Lecturers: **Dr. Dare, E. O. (B. Sc., M. Sc., Ph D)**

COURSE CONTENT:

Principal series of organic compounds: Allicyclic (Acyclic aliphatic, cyclic, carboxylic, aromatic and heterocyclic hydrocarbons (mere treating and classification).
Structure of benzene and aromaticity.
Functional group Chemistry: Alcohol, Phenols, Amines, carbonyl compounds, acids; α,β-unsaturated compounds and their derivatives.
Introduction to Organic reaction types: Substitution, Elimination, addition and re-arrangement.

COURSE REQUIREMENTS:

This is a compulsory course for 300 level students in the Departments of Chemistr. In this respect, students are expected to participate in all the course activities and have minimum of 75% attendance to be able to write the final examination.

READING LIST:

1. George, H., Schmid. Organic Chemistry, New York, Mosby, 1995.

LECTURE NOTES

PESTICIDES

The term pesticide refers to toxic/poisonous chemicals which are used directly or indirectly against pests or insects in order to eradicate or control such pests. Pesticidal compounds are often used in the control of pests and diseases of plants and to control of micro-organisms and other microbes that disturbs the growth and productivity in plants. The are generally known to be toxic.

Pesticides include:

1. Insecticides – used against insects

2. Herbicides – used against weeds
3. Rodenticides- used against rodents
4. Bacteriocides – used against bacteria
5. Nematocides – used against nematodes
6. Molluscides – used against mollusk
7. Nematocides – used against nematodes
8. Algicides- used against algae
9. Fungicides –used against fungi.

Importance of Pesticides

Since historical time, there were concerted efforts by man to produce food for the ever growing world's population. In spite of the rapid technological development, still the end has not justified the means in the area of food production. The report of World Health Organization indicated that a third of the population of the world suffer from hunger and malnutrition. This is because agricultural production faces some problems emanating from invasion by pests, weeds, microbial infections, etc. Pests equally attack stored grains, tubers, to the extent that they cause a lot of damage. A complete elimination of the problem above was achieved through by integrated pests management which includes quarantine, agro technical, mechanical, biological and chemical methods. The chemical methods of protecting agricultural products as well as the animals was based on the use of various organic and inorganic compounds which are synthesised and are known to be toxic to pests invading plants and animal outreach. It is important to note that pesticides cannot increase the plant yield, but have ability of eliminating pests that can impair plant growth. The use of pesticides started after the Second World War.

Historically, the earliest pesticidal compound ate mostly inorganic compounds such as $CuAs_2O_3$ (copper arsenate), sulphur compounds as well as naturally-occurring rotenone and pyrethroids. $CuAs_2O_3$ has been used to eradicate colorab that infects tomato while sulphur compounds are used as insect repellants. After this, then comes natural pesticides; some were obtained from plant extract e.g. nicotine obtained from tobacco leaves; pyrethroids obtained from pyrethrin flowers. Then come synthetic pesticide which includes:

1. Organochlorine pesticides;
2. Organophosphorous pesticides;
3. Organocarbamates and
3. Synthetic Pyrethroids.

Reasons for the obsolescence of pesticides

Generally, majority of used insecticides often turns obsolete and functionless after some time, due to some peculiar problems associated with them. Some of this issue has to do with the adaptability of some organisms to environment. The toxic nature of some chemicals to animate and inanimate substances led to their total ban and usage, especially those that have genetic effects such as genetic mutation.

Development of new pesticides that is cheaper and less hazardous to the applicant, consumer or even the environment. High specificity and selectivity of these chemicals to the environment is another factor in favour of new insecticides produced on regular basis.

Properties or characteristics of pesticides

1. They are toxic and therefore constitute pollutant materials into the atmosphere e.g. organochlorine pesticides;
2. Most pesticides have simpler structure, with simple biological activities.
3. Each pesticide has a lethal dose (LD_{50})
4. Each pesticide has chemical intermediate, which often get obsolete after some time.

Regulations on the use of pesticides

As a result of the toxic and hazardous nature of most pesticides to animals and inanimate substances, when disposed carelessly, regulations on the use of pesticides have been enacted. Regulatory bodies such as Federal Environmental Protection Agency (FEPA) in Nigeria have enacted laws to regulate the use of pesticides. The law has to do with the need to protect the operators and the public against dangerous effects of pesticides or effects of the residues of some pesticides. The law involves complete banning and shipping of certain pesticides to and fro Nigeria. It equally involves standardization of manufactured chemicals and protection of the consumers of finished products. The same regulation includes a provision that protects the supplier of toxic chemicals, application of toxic chemical and other personnel proximal to the use of pesticides.

Classification of pesticides

Generally, pesticides are classified into natural and synthetic ones.

1. Natural Pesticides include Pyrethroids, Nicotine and Rotenones
2. Synthetic Pesticides include Organochlorines, Organophosphorous, Organocarbamates and Synthetic Pyrethroids.

Various methods have been used to classify pesticides, as shown below:

1. Classification based on intended use or the target organisms;
2. Classifications based on the chemical nature of pesticide or simply on the chemical compositions. Chemical classification of pesticides is in three categories viz:

(a). Inorganic compounds such as sulphur and $CuAs_2O_3$, mercury and ;

(b). Natural pesticides or botanical pesticides-are those derived from vegetable plants, bacteria of from fungi preparation

(c). Synthetic organic compounds such as Organochlorine, Organophosphorous, Organocarbamates and Synthetic Pyrethroids .

3. Classifications based on the mode of action – this depends on how the poison penetrates or permeates into the body of the pests and consequently knocking it down. Some sub-classification under this are enumerated below:

(a). Stomach poison pesticides: acts by poisoning insects when swallowed and digested with the food;

(b). Contact poison insecticides: acts by poisoning the insect when in contact with the skin;

(c). Fumigants: acts by penetrating the organisms through respiratory tracts in the form of gas or vapour. They are basically vapour phase chemicals and are usually applied as aerosols.

The stomach and fumigant pesticides are generally called systemic chemicals.

Important Characteristics of Pesticides

An ideal pesticide possesses two major characteristics viz:

(a). Specificity: an ideal pesticide must be specific in its action, that is it should attack only the targeted species or organisms or pests;

(b). Non-persistent: an ideal pesticide must be readily degraded in the environment within few days or weeks and should not partition into the adipose tissue or leaves residues that impair ecosystem.

Generally, ideal pesticidal compounds must be cheaper, have low toxicity to applicants and should be easy to apply.

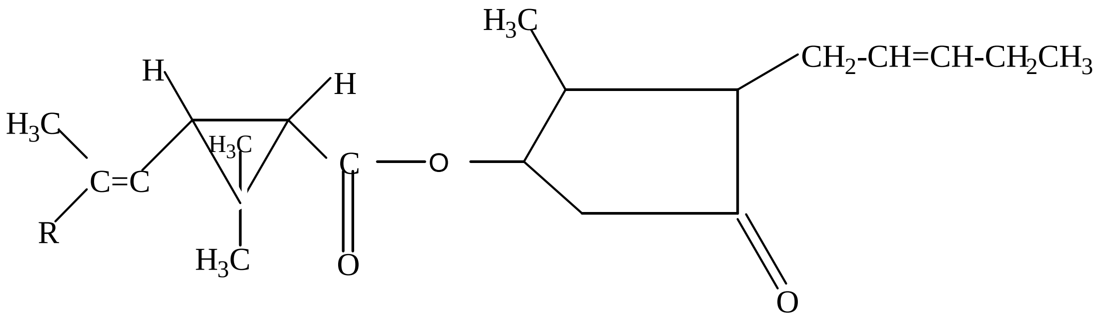
Natural Pesticides

An example of natural pesticides, also called botanical pesticides is pyrethroid. It is extracted from pyrethrum plant using petroleum ether or acetone. Natural pesticides are often characterised by a reasonable knock-down effect of flies. Often, they are used as domestic spray against flies and mosquitoes. They have extremely low toxicity on warm-blooded animals. They are less persistent to the environment because they re rapidly destroyed light, and are said to be photodegradable. They are contact poison pesticide and are equally neurotoxin. Generally, pyrethroids are broad spectrum insecticide, hence they eradicate beneficial insects.

Chemistry of Natural Pesticides

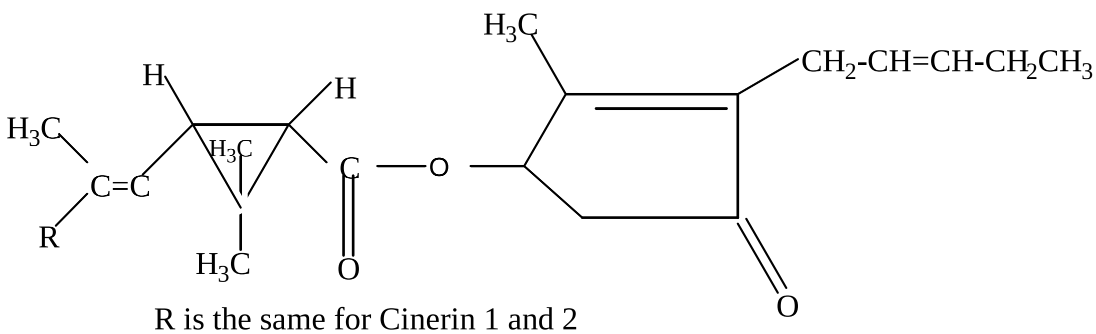
Basically, natural pesticides contain four principal ingredients known as pyrethrin 1 and 2, and cinerin 1 and 2.

PYRETHRIN



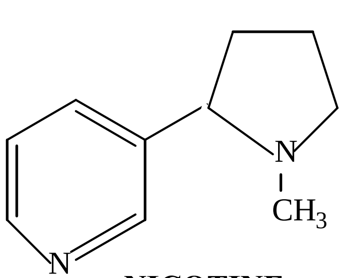
Pyrethrin 1-R=CH_3
Pyrethrin 2-R=$COOCH_3$

CINERIN

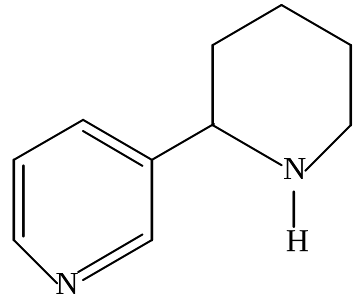


R is the same for Cinerin 1 and 2

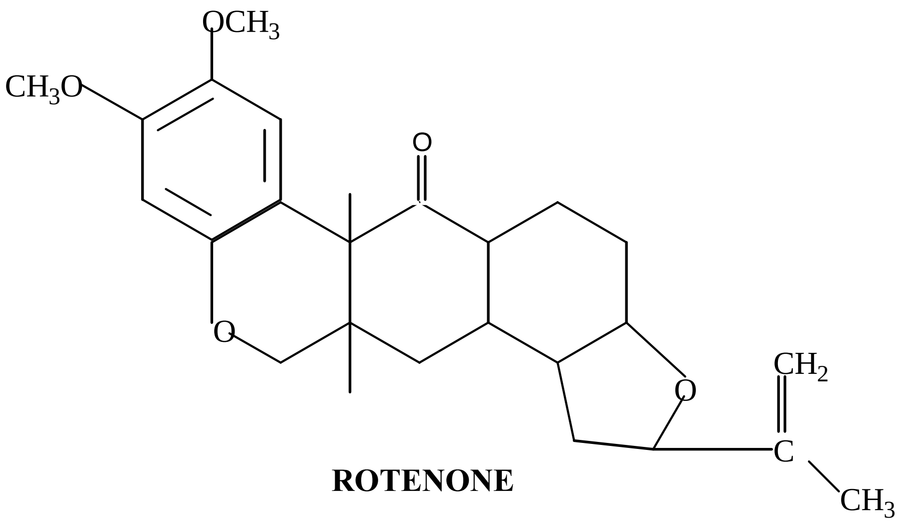
Other examples of natural pesticides are Anabasine, Nicotine and Rotenone



NICOTINE



ANABSINE

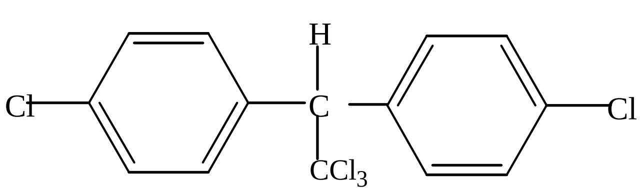


ROTENONE

SYNTHETIC ORGANIC INSECTICIDES

Organochlorine Insecticdes

A common feature of all organochlorine insecticide/compounds is the presence of chlorinated carboxylic ring in the structure of the molecule Another peculiar feature of organochlorine is their low water solubility (hydrophobicity) hence they are strongly lipophilic. Consequent upon their solubility, they are often retained in body fat and as such, they are rarely degradable into extractable water, hence they are accumulated in the adipose tissues. They are generally known as bio accumulator. Organochlorine compounds are waxy at room temperature. Common example of organochlorine pesticides is dichlorodiphenyltrichloro ethane (DDT). Its IUPAC name is 1,1,1-trichloro-2,2-bis-p-chlorophenyl ethane.

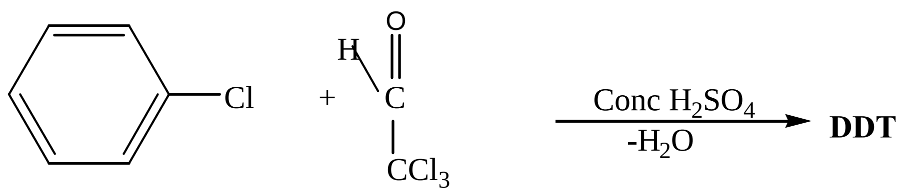


Structure of DDT

Zeilder prepared DDT without an idea of its potential insecticidal properties. This property was discovered later by Paul Miller in 1939. He discovered that DDT was very effective against mosquito housefly and bed bugs. In other word, DDT was found to be a broad spectrum insecticide, it is not selective. This earns him a Nobel prize in 1948.

Preparation of DDT

DDT is readily prepared from phenyl chloride and 1,1,1-trichloroethanal (chloral). DDT was the first synthetic insecticide known. The reaction is illustrated below



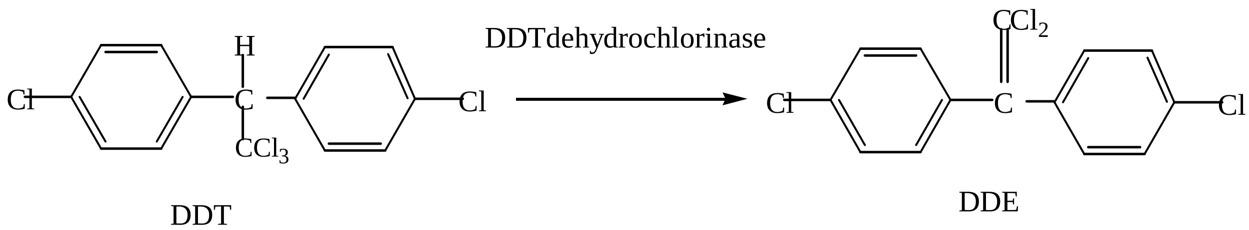
DDT is abroad spectrum organochlorine insecticide. It has several methods of synthesis. It has been used specifically for soil insect control, malarial eradication through killing of mosquitoes. It is also used for the control of termites.

Physical properties of DDT

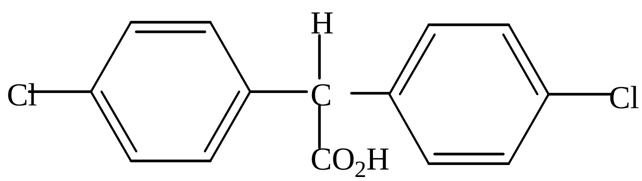
A technical grade DDT is a volatile waxy solid with melting points of 90oC. The para-para DDT is a white powder with a melting point of 110^{o}C, insoluble in water.

Insecticidal properties of DDT

DDT has broad spectrum insecticidal activities, killing variety of insects and used specifically against mosquito-transmitting malarial parasites and other flies that transmits typhoid. Despite its broad spectrum insecticidal usage, DDT is known to be insoluble in water; hence it does not get degraded fast in the environment, resulting into partitioning into the body fat. This has led to the total ban of DDT in advanced countries; though it is still widely used in developing nations, where environmental control and monitoring is not effective. A major disadvantage of DDT and its analogue is that it is readily detoxified by some insects that are resistant to it; e.g. DDT can be converted easily to Diphenyl dichloro ethylene (DDE). This conversion is aided by an enzyme known as DDTdehydrochlorinase e.g.



Once DDT is converted to DDE, it becomes inactive. In other words, certain insects have developed enzymedehydrochlorinase. In mammals and birds, DDE is further converted to diphenyldichloroacetic acid (DDA).



DDA

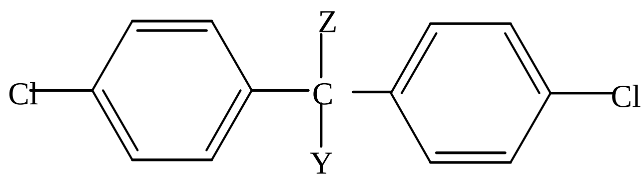
Mode of actions of DDT

Insecticidal activity of DDT is due to the fact that they interfere with the transmission of nerve impulses in insects, thereby interrupting or upsetting the K^+ and Na^+ balance of their nerve membrane.

Toxicology of DDT

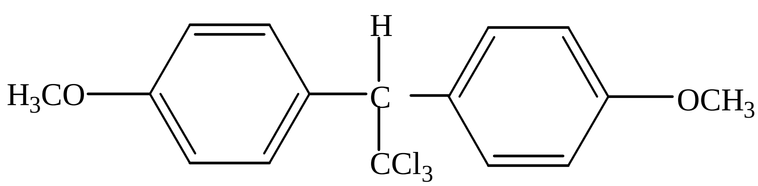
Organochlorine varies widely in their toxicological activities, and acute toxicity to mammals and insects. Some acute oral doses of LD_{50} are known. Action of DDT in mammal is through disruption of the nerve connection and since they are slowly metabolized and lipophilic, they partition into the body fat, hence frequent exposure must be avoided. There have been reported cases of accidental killing of birds, fish and other non-targeted species such as egg shell thinning in species near the top of the food chain.

Other polychlorobiphenyl insecticides



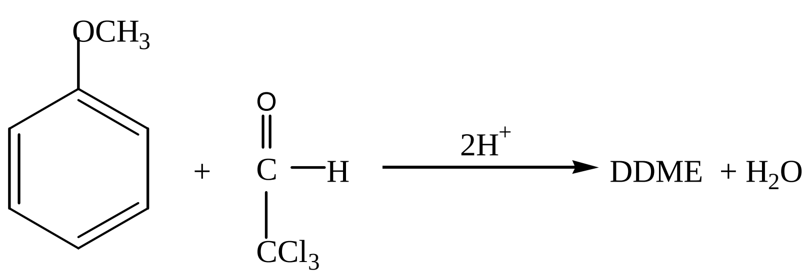
Y =CCl_2, Z = H= DDE

Y = CO_2H , Z = H =DDA
Y =CCl_3, Z = H+ = DDT
Y = C=O-OC_2H_5, Z = OH = Dicofol



DDME

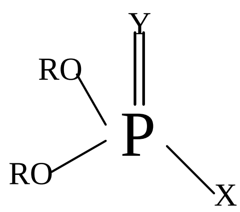
DDME is called methoxylchloro. Its preparation is via condensation of chloral and methoxyl benzene (anisole):



DDME has low mammalian toxicity and has been found to be more active in the control of insects that attack livestock, fruits and vegetables. It has low mammalian toxicity, with lower tendency to be stored in the body fat of animals. This is as a result of their high solubility in water. It is a pro-organochlorine insecticide known for its less toxicity compare to DDT. Hence, DDME is a good insecticide for livestock treatment. The presence of methoxyl group surrounding the side chains of the benzene ring, account for its high solubility. DDME is resistant to heat, UV radiation and oxidation.

ORGANOPHOSPHATES

General feature of organophosphate insecticide is represented thus:

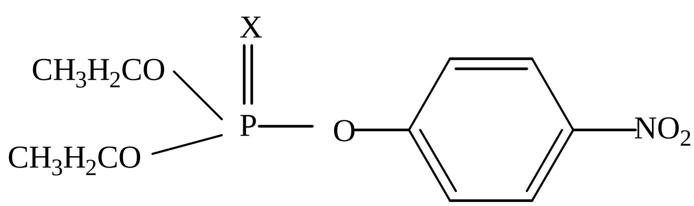


R = Alkyl group
X = Phenyl group

Key

Y =O = Paroxon,
Y = S = Parathion

Specific examples are illustrated below:



O,O-diethyl-4-nitrophenylphosphoroparoxon, X = O

X = S - Parathion

X = O - Paraoxon

Organophosphorous insecticides many organic compounds based on the fact that they are simple esters of monophosphorous compounds. Over 100 organophosphorous compounds have been marketed. They were developed by German scientists after the Second World War. Different members of organophosphorous insecticides possess different physical and chemical properties. They vary widely in solubility in water, but in most cases they are very soluble in water. They equally vary in their stability and toxicity to mammal. The wide spectrum of their physicochemical and biological properties made them to be widely useful in agriculture and natural hygiene. Some are used as fumigants; others are used as contact poison and for crop protection in their early growing season. In most cases, they are used n plants such as sorghum, corn, cotton, rice, wheat, barley and soybeans. They are equally used in crop fruits and vegetables for foliage and root protection. In veterinary outlook, they are used against ectoparasites control in cattle and sheep, in the form of ear tag, spray or dip. As a result of their environmental acceptability, they have specific modes of actions. They are relatively unstable in biological systems (not persistent).

Chemistry of Organophosphate

The phosphorous atom is electrophilic, owing to the depolarization of P=O bond and partly due to the electron-withdrawing nature of para - nitro phenyl moiety. This enhances its high solubility in water.

Mode of action of Organophosphate insecticide

The nature of the phenyl group arising from the electron-withdrawing property of the phenyl group makes the phosphorous atom electrophilic, hence its ability to phosphorylate nucleophile such as co-enzyme A and also, the 4-nitro phenyl moiety is a good leaving group.

Toxicology of Organophosphorous insecticides

Mechanism of action of organophosphorous insecticides in mammals and insects are similar. Poisoning action is caused by toxification of the acetycholine stearase . Killing in animal is due to paralysis of striated respiratory centre. However, the most effective antidote is to organophosphate poisoning is atropine, which blocks acetycholine receptors of the motor end of plate of the para sympathetic nervous system, that controls the respiratory muscle. Generally, organophosphorous are less toxic compare to organochlorine insecticide. The y do not persist in the environment and are water – soluble compare to DDT.