CLASSIFICATION OF INSECTICIDES

Prof. Dr. Farkhanda Manzoor

Head of Zoology Department

Lahore College for Women University

Lahore

History And General Groupings Of Insecticidal Compounds

Evolution of chemical insecticides essentially began with readily available materials such as arsenicals, petroleum oils, and botanical insecticides (e.g., nicotine, pyrethrin, rotenone).

The first synthetic organic insecticides that appeared for public use were dinitro compounds and thiocyanates.

The most significant discovery leading to the proliferation of new synthetic insecticides was that of DDT.

This unusual compound, 1,1,1- trichloro-2,2-bis(p-chlorophenyl)ethane, was first synthesized by Zeidler in 1874, but its insecticidal properties were first discovered in 1939 by Muller of Switzerland. The use of DDT revolutionized the control of insect pests.

Other chlorinated hydrocarbon insecticides such as BHC, toxaphene chlordane, aldrin, and dieldrin followed immediately thereafter.

The second massive introduction of new insecticides was initiated by a German worker, Gerhard Schrader, a pioneer in the chemistry and uses of organophosphorus insecticides.

The number of organophosphorus compounds (OP compounds) used for insect control today is unmatched by any other group of insecticides.

The most widely used organophosphorus compounds include parathion, Systox, malathion, EPN, diazinon, and DDVP (dichlorvos).

The carbamates are a relatively new group of synthetic insecticides. These compounds (essentially the synthetic analogues of an important alkaloid poison, physostigmine or eserine) were first developed by the Geigy Company for insecticidal use in 1947.

For all practical purposes, insecticides include activators and synergists, chemosterilants, and hormonal agents, which may not directly kill insects by themselves.

Chlorinated Hydrocarbon Insecticides

The chlorinated hydrocarbon compounds include such important insecticides as DDT, BHC, chlordane, and dieldrin.

All compounds which belong to this group are characterized by:

(1) The presence of carbon, chlorine, hydrogen, and sometimes oxygen atoms, including a number of C-C1 bonds.

(2) The presence of cyclic carbon chains (including benzene rings)

(3) Lack of any particular active intramolecular sites.

(4) Apolarity and Iipophilicity.

(5) Chemical unreactivity (i.e., they are stable in the environment).

These chemicals are often considered to belong to the group of organochlorine pesticides.

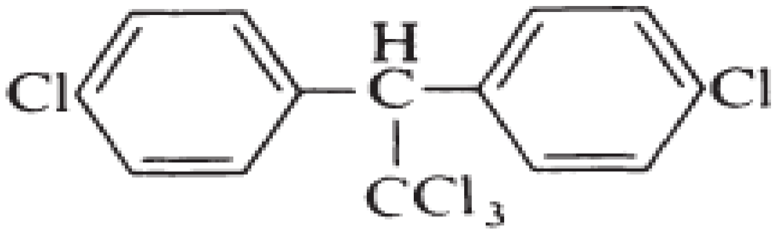
However, their group characteristics make them very different from other organochlorine pesticides such as fumigants, chlorinated organophosphates (e.g., Dursban), carbamates, and chlorinated aliphatic and aromatic acids.

There are three major kinds of chlorinated hydrocarbon insecticides:

- DDT analogues
- Benzene hexachloride (BHC) isomers
- Cyclodiene compounds

DDT and Its Analogues

DDT is one of the most important insecticides ever to appear on the market. Its chemical structure is:



1,1,1-TRICHLORO-2,2-BIS(*p*-CHLOROPHENYL)ETHANE

It can also be called dichlorodiphenyltrichloroethane, hence DDT.

DDT is a white to cream-colored amorphous waxy powder, and pure DDT is a crystalline powder.

The melting point of the pure compound is 109°C, and its setting point (crystallization on slow cooling) is between 103° and 105°C. Technical DDT has a melting point of 89°C and is considered a satisfactory product if its setting point is not below 88°C.

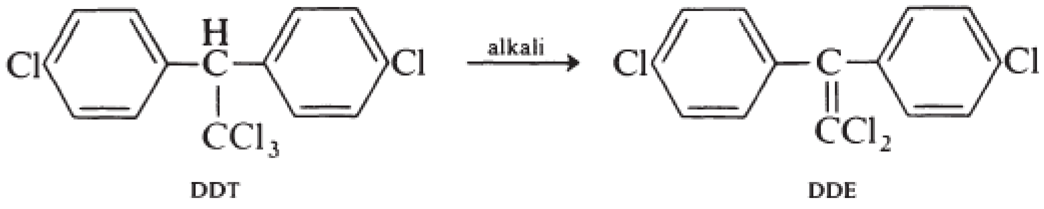
DDT is one of the most apolar compounds known to exist; hence it is soluble in most apolar organic solvents and is practically insoluble in water and cold ethanol.

Its water solubility is less than 2 ppb (parts per billion). Since DDT is soluble in hot ethanol, it can be recrystallized by cooling ethanol in which DDT has been dissolved.

The solubility of DDT in most solvents rises steeply with increase in temperature.

The average commercial product contains about 70 % of the pure p,p'-DDT. Increasing the amount of chloral used in DDT preparation increases the purity of the product. The major contaminant of crude DDT is o,p-DDT, which is not as insecticidal as p,p'-DDT.

DDT is very stable, chemically as well as biochemically, except in the presence of alcoholic alkali, which dehydrochlorinates it to form dichlorodiphenyldichloroethylene, known as DOE, which is nontoxic to insects. Traces of iron, aluminum, or chromium salts catalyze this reaction.



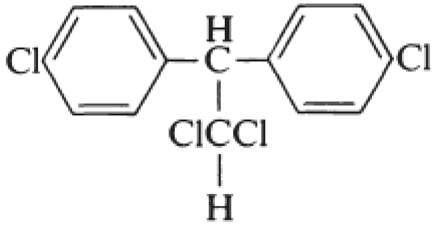
Solid-form DDT is not decomposed by sunlight or ultraviolet light, but residues of powdered DDT under field conditions with maximum surface exposure and ultraviolet irradiation are slowly decomposed into non-insecticidal components.

Tropical temperatures and high relative humidity cause DDT dusts to lose their toxicity at faster rates, but hot, dry weather also increases loss, probably by raising its volatility.

Pure DDT is stable to the action of heat and does not decompose below 195°C; however, technical DDT decomposes at about 100°C due to the presence of impurities. DDT has a low vapor pressure of 1.5 x 10- 7 mm Hg at 20°e.

TDE (DDD)

An important DDT analogue widely used to control various kinds of insect pests is TDE.



1,1-DICHLORO-2,2-BIS(*p*-CHLOROPHENYL)ETHANE

This insecticide is sometimes called dichlorodiphenyldichloroethane (hence DDD) or tetrachlorodiphenylethane (hence TDE).

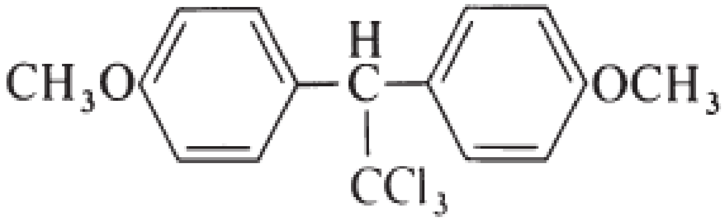
Pure TDE is a white crystalline solid with a melting point of 109°C, and the technical product has a setting point of 86°C. It has a sweet odor.

Its solubility is similar to that of DDT, but it is dehydrochlorinated in alkali at a slower rate than DDT.

In general, TDE is less effective than DDT for controlling insects, with some exceptions. It is superior to DDT for controlling black fly larvae, red-banded and fruit tree leaf rollers, tomato and tobacco horn worms, and the Mexican bean beetle. It is 1/5 to 1/10 as toxic as DDT to mammals, with an oral LDso in rats of 3400 mg/kg.

Methoxychlor

Another important DDT analogue is methoxychlor (DMDT, or methoxy-DDT).



1,1,1-TRICHLORO-2,2-BIS(*p*-METHOXYPHENYL)ETHANE

Methoxychlor is a white crystalline solid with a melting point of 89°C. Technical methoxychlor is a pale buff to gray flaky powder and has a setting point of 69°C. The water solubility is quoted as 0.1 ppm and it is soluble in most organic solvents and subject to dehydrochlorination.

Methoxychlor is only 1/25 to 1/50 as toxic as DDT to mammals. It has an LDso in rats of 6000 mg/kg, which makes it essentially nontoxic. It is not accumulated in fatty tissue or excreted in milk as DDT is.

Therefore, methoxychlor is preferred to DDT for use on animals, in animal feed, and in barns. Since methoxychlor is more unstable than DDT, it has less residual effect. Compared to DDT, methoxychlor is more toxic to some insects and less toxic to others.

It has a faster knockdown of houseflies than DDT.

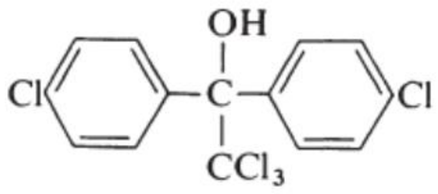
Dicofol

Mites and ticks (class Arachnida, order Acarina) are not insects, their control is within the realm of the entomologist; chemicals used for this purpose are called acaricides.

When the use of DDT became widespread, mite and tick populations often increased since DDT killed their natural predators, the insects, while not harming them. Many acaricides were developed and tested during World War II as clothing and skin repellants and toxicants against the mite vector of scrub typhus.

There are several DDT analogues which are effective acaricides and nontoxic to insects. One of these, dicofol, is also a major metabolite of DDT from Drosophila and German cockroaches (Blattella germanica). Dicofol is also known by the commercial name Kelthane.

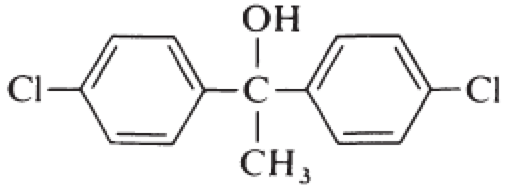
Dicofol is a brown, viscous oil which is soluble in most organic solvents. It is slightly more soluble in water than DDT. It is moderately toxic, with an oral LD50 in rats of 575 mg/kg.



4,4′-DICHLORO-α-(TRICHLOROMETHYL)BENZHYDROL

DMC (DCPC)

A DDT analogue effective against both eggs and active stages of many mite species is DMC, marketed as Dimite.



4,4´-DICHLORO-α-METHYLBENZHYDROL

DMC is a colorless, crystalline solid with a melting point of 70°C.

It is decomposed by acid, is stable in alkaline solutions, and is soluble in organic solvents. It is not easily manufactured and is therefore expensive.

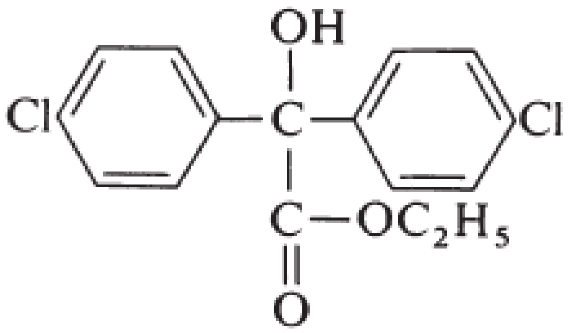
DMC, which has a moderate residual effect, kills slowly and produces a semiparalysis of the mite.

DMC can also be used to inhibit the ability of DDT-resistant houseflies to dehydrochlorinate DDT.

However, such flies are able to develop more enzyme to overcome the effect of DMC. Its oral LDso in rats is 926-1391 mg/kg.

CHLOROBENZILATE

Another DDT analogue which has been used as an acaricide is Chlorobenzilate.



ETHYL 4,4′-DICHLOROBENZILATE

Chlorobenzilate is a yellow crystalline solid with a melting point of 35-37°e.

It is soluble in most organic solvents and slightly soluble in water.

It is hydrolyzed by alkalis and strong acids. It is not generally toxic to insects.

Residues of this material are known to be persistent in the field. Its mammalian toxicitsy (rat, oral LD50) is 3100-4850 mg/kg.