

d. Organochlorine compounds:

Simple hydrocarbons like naphthalene has a long history. It was used for protection of timber from boring insects and as a repelling agent for lice in men and domestic animals. However, the major pesti-
cidal importance of the hydrocarbons does not lie in simple com-
pounds. Their utility as pesticides increased enormously by the intro-
duction of halogen atom particularly chlorine or bromine into their
molecule. Even the simplest hydrocarbon such as methane (CH_4) is
transformed into extremely valuable pesticide by the substitution of
halogen atom. Methyl bromide (CH_3Br) is the example which is widely
used in ships, mills and warehouses for the destruction of stored grain
pests. Another example is ethylene dibromide ($\text{C}_2\text{H}_4\text{Br}_2$) which was ob-
tained by substituting two bromine atoms in ethane (C_2H_6). This com-
pound has gained much popularity as a fumigant.

The organochlorine compounds can further be classified under the following groups according to their molecular structures:

1 — Diphenyl methane structure: Where two benzene rings are attached to a single external carbon atom e.g. DDT and related compounds.



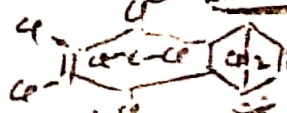
2 — Monocyclic structure: Where there is only one non-aromatic hydrocarbon ring e.g. BHC, Lindane.



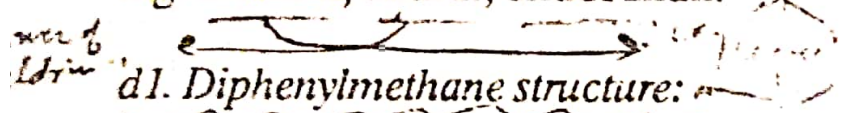
3 — Bicyclic structure: When two non-aromatic hydrocarbon rings are fused together so as to have two non-adjacent carbon atoms to both rings e.g. toxaphene.



4 — Polycyclic structure: Where three or four non-aromatic hydrocarbon rings are fused at least at two points e.g. aldrin, chlordane, heptachlore.



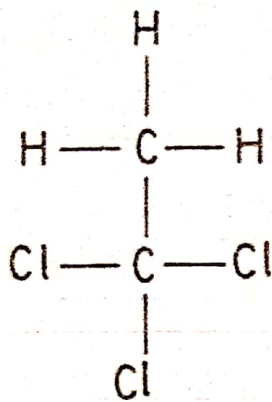
5 — Heterocyclic structure: Where there is one or more rings of non-aromatic hydrocarbon and at least one of the atoms in one of the rings is not a carbon atom it makes a heterocyclic structure. (may be N, O, S) e.g. dieldrin, endrin, endosulfan.



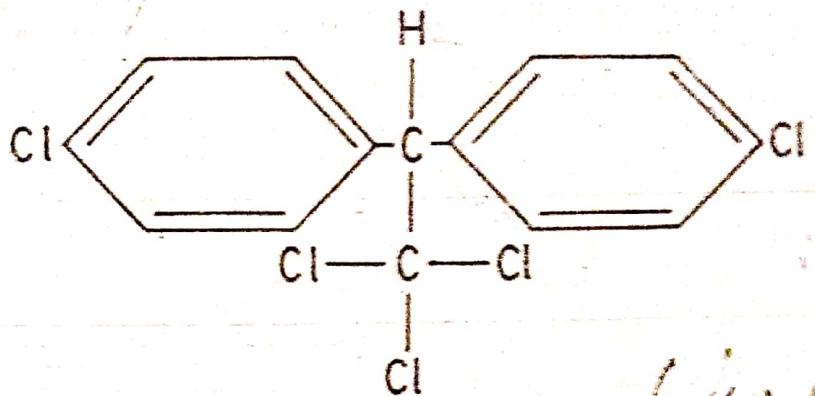
note of Aldrin

d1. Diphenylmethane structure:

DDT: $C_{14}H_9Cl_5$: dichlorodiphenyl trichloroethane. It was first synthesized by Zeidler in 1874 but its insecticidal properties were discovered by Paul Muller in 1939. Substitution of two chlorophenyl groups into the molecule of trichloroethane gives DDT. Technical DDT is a white to cream coloured amorphous powder and has a variable composition of about 14 compounds of which the isomer p-p' DDT (65 to 80%) and o-p DDT (15 to 20%) form the chief constituents. The proper chemical name is 1, 1, 1-trichloro-2,2-bis- (p-chlorophenyl) ethane. Highly purified DDT is quite stable and does not decompose below $195^\circ C$ but technical material readily decomposes at about $100^\circ C$ due to the presence of impurities such as iron which acts as a catalyst. The decomposition of DDT residues may be attributed to two reactions (i) dehydrochlorination by alkali in which it is converted into non-insecticidal product 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene. (ii) Oxidation in which it is oxidised to p,p -dichlorobenzophenone in the presence of ultra-violet light.



Trichloroethane

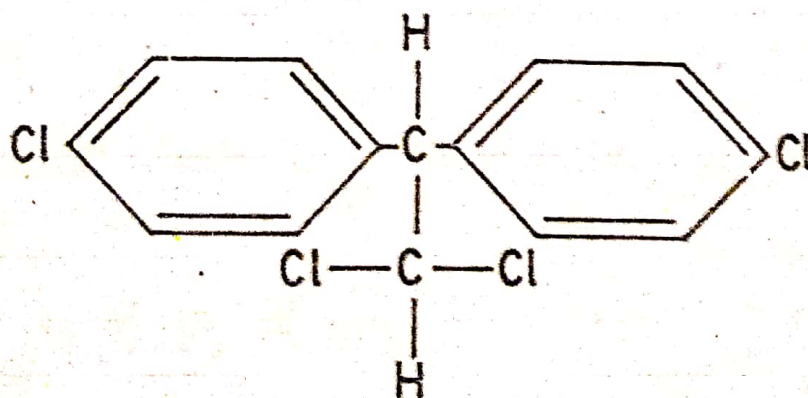


DDT

DDT is the most durable of all the insecticides commonly used today due to its insolubility in water, very low vapour pressure and its resistance to light and oxidation. Residues of DDT may remain effective for a longer period. It is relatively slow-acting insecticide. The use of DDT on animal forage crops is discouraged because of its accumulation in the fat of animals. It is phytotoxic to cucurbits.

Analogues of DDT: Several analogues of DDT have insecticidal properties:

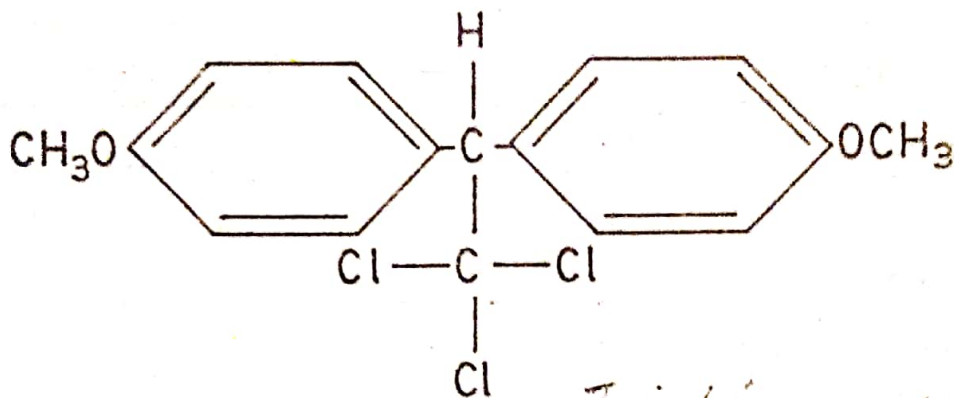
DDD: $\text{C}_{14}\text{H}_{10}\text{Cl}_4$: dichloro diphenyl dichloroethane or TDE; tetrachloro diphenyl ethane. It is less effective than DDT but it has an advantage of being less toxic to warm blooded animals and fishes. It is superior to DDT for the control of mosquito larvae.



DDD

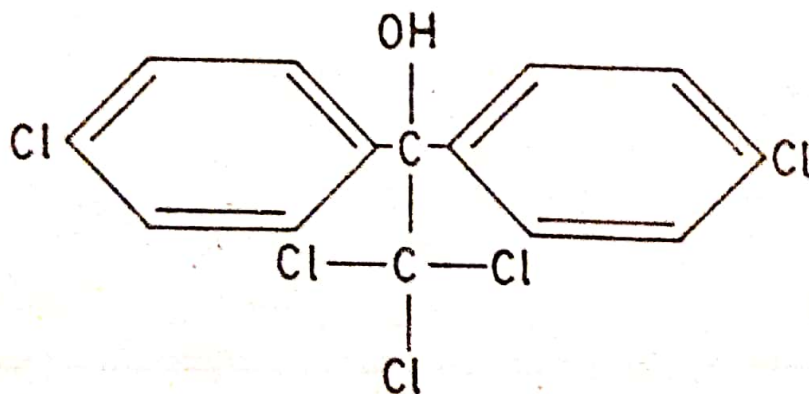
Methoxychlor: $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Cl}_3$: 1,1,1-trichloro-2,2-bis(p-methoxy phenyl) ethane. The replacement of p-chlorine of DDT by methoxy group (OCH_3) gives methoxychlor which has more rapid knockdown than DDT. Its LD_{50} in rats is very high (6000 mg/kg) which makes it safer than DDT. It is not accumulated in fatty tissues. Therefore, it is

preferred to DDT for use on animals. Since it is more unstable, it has less residual effect. The technical compound is white crystalline with m.p. 70-85°C. Its dehydrochlorination takes place like DDT but slowly.



Methoxychlor

Dicofol: $C_{14}H_9Cl_5O$: 1,1-bis (p-chlorophenyl)-2,2,2-trichloro ethanol. It was introduced in 1955 under the trade name 'Kelthane'. It is an acaricide harmless to bees.

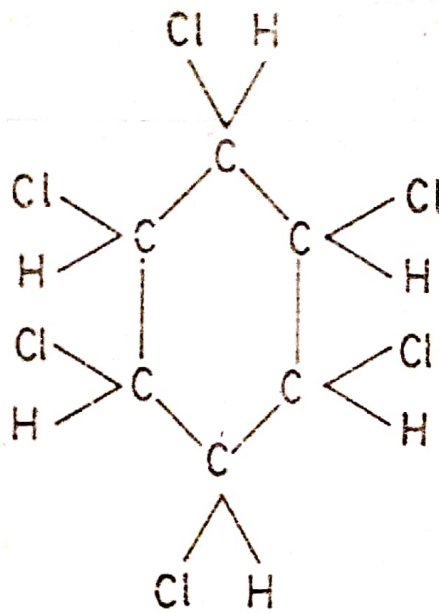


Dicofol

d2. Monocyclic Structure:

BHC: $C_6H_6Cl_6$: 1,2,3,4,5,6-hexachlorocyclohexane. The compound was first synthesized by Faraday in 1825. Its insecticidal properties were discovered by British and French workers independently between 1940 and 1942. In 1943 it was made known that the active principle of technical **BHC** is gamma isomer which was isolated by Van der Linden, a German chemist in 1912. The 99% pure gamma isomer is called lindane after his name. BHC contains 10 to 80% of active gamma

isomer together with four other isomers of varying proportions: alpha-55 to 70%, beta-5 to 14%, delta-6 to 8% and epsilon-3 to 4%. Beta and epsilon are non-toxic.



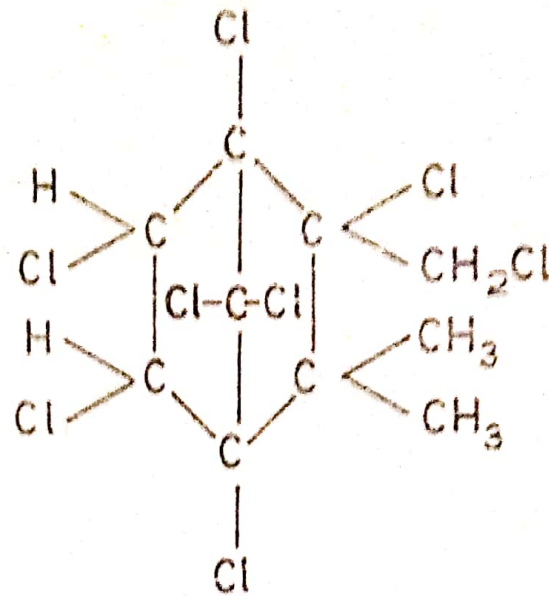
BHC

The crude product is greyish or brownish amorphous solid with a very characteristic musty odour having melting point 65°C. The pure gamma isomer has slightly aromatic odour. It is very stable to the action of heat and oxidation but readily decomposed by alkali materials to form 1,2,3- and 1,3,5-trichlorobenzene and HCl (dehydrochlorination). Unlike DDT, both BHC and lindane have higher vapour pressure, therefore, they also exhibit fumigant action in addition to their contact and stomach poison activity. The main disadvantage of commercial BHC preparation is that several fruits and vegetables pick up an unpleasant odour or taste from BHC application but this disadvantage can be overcome by the use of lindane in place of BHC.

d3. Bicyclic structure or chlorinated terpenes:

Toxaphene: C₁₀H₁₀Cl₈ : It is prepared by chlorination of bicyclic terpene. It was introduced in 1948. The technical material is yellowish semi-crystalline gum with melting point 65 to 90°C. It is unstable in the presence of alkali. Prolonged exposure to sunlight and temperature above 155°C liberate hydrogen chloride from this insecticide; this causes loss of its insecticidal property. To tie up hydrogen chloride evolved in storage small amount of epichlorohydrin is added for stabilization of the active ingredient of the insecticide. It is a persistent contact and

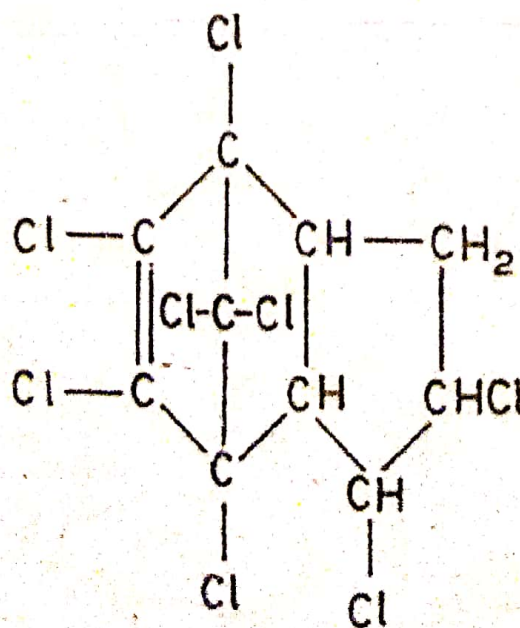
stomach poison having less residual action than DDT. It is less toxic to bees.



Toxaphene

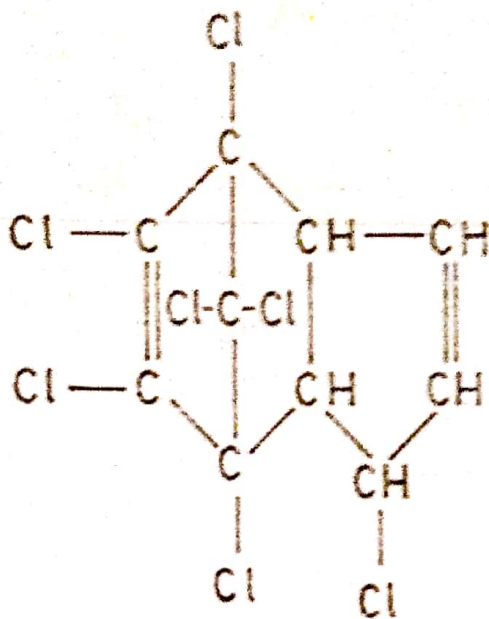
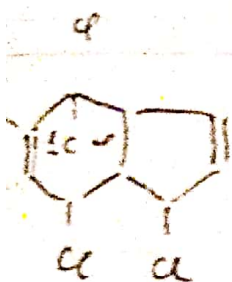
d4. Polycyclic structure:

Chlordane: C₁₀H₆Cl₈ : It was discovered by Hyman but its insecticidal properties were described by Kearns and his associates in 1945. Chemically it is composed of two isomers alpha and beta of chlordane and two isomers of heptachlor in 60,40 ratio. The heptachlor is present as contaminant. The technical material is a brown, viscous liquid with an odour resembling cedar. It is persistent stomach and contact insecticide having a light fumigant action. It is very toxic to bees. Like toxaphene it also liberates HCl under the influence of alkali; hence addition of stabilizer is necessary in the insecticidal formulation.



Chlordane

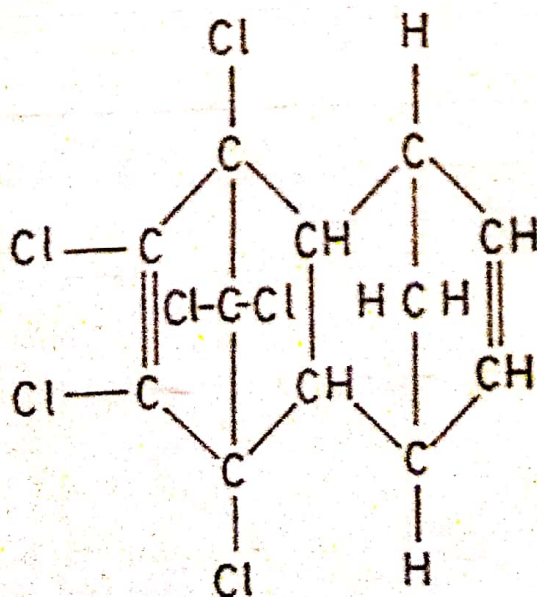
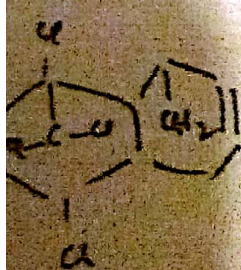
Heptachlor: $C_{10}H_5Cl_7$: It was introduced in 1948. The pure compound is white crystalline whereas the technical grade is waxy



Heptachlor

mass with melting point $46-70^{\circ}C$ containing 65 to 72% heptachlor. It is 3 to 5 times as toxic to insects as chlordane. In animals, plants and insect tissues heptachlor is converted to its epoxide which is more insecticidal than the parent compound. It is a powerful stomach and contact poison with some fumigating property.

Aldrin: $C_{12}H_8Cl_6$: In 1949 Kearns and his associates discovered the toxic properties of aldrin. It was named after a German chemist Kurt Alder who got Nobel Prize in chemistry in 1950 alongwith his co-worker Otto Diels for the work on diene synthesis. Their Diel-Alder reaction is very famous and is used in formulation of cyclodienes. The technical material is a tan to brown solid containing about 78% active aldrin. The pure material is white crystalline with melting point $104^{\circ}C$.

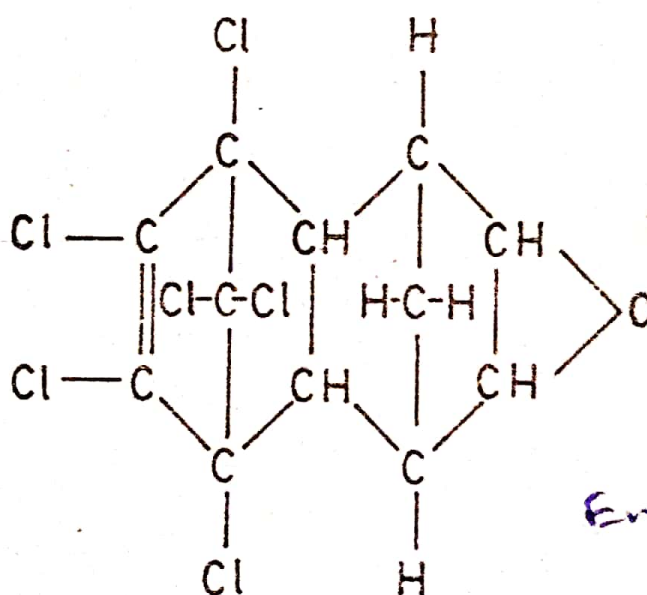


Aldrin

The impurities in technical material slowly form HCl in storage hence epichlorohydrin which inhibits acid is added as stabilizer. It is oxidised to its epoxide dieldrin within soil, insect body and in the liver of animals.

d5 Heterocyclic structure:

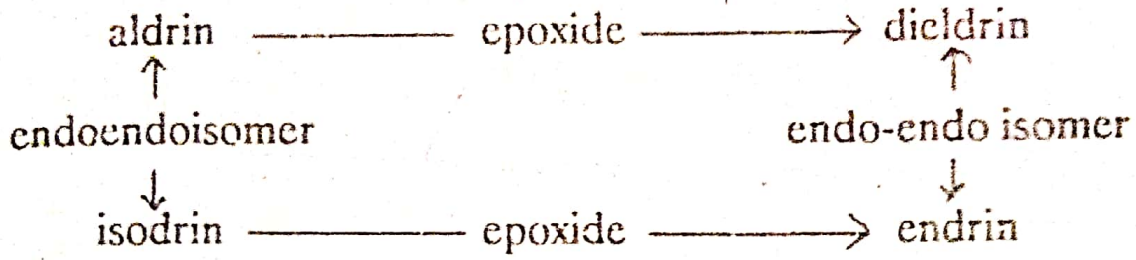
Dieldrin: $C_{12}H_8Cl_6O$: Like aldrin it was also discovered by Kearns and his associates in 1949 and named after German chemist Otto Diels. It is the epoxide of aldrin. The pure compound is odourless white crystalline solid while the technical material is a flaky tan solid containing about 76% dieldrin. It is a persistent insecticide of high contact and stomach insecticidal activity. It is very effective against soil pests.



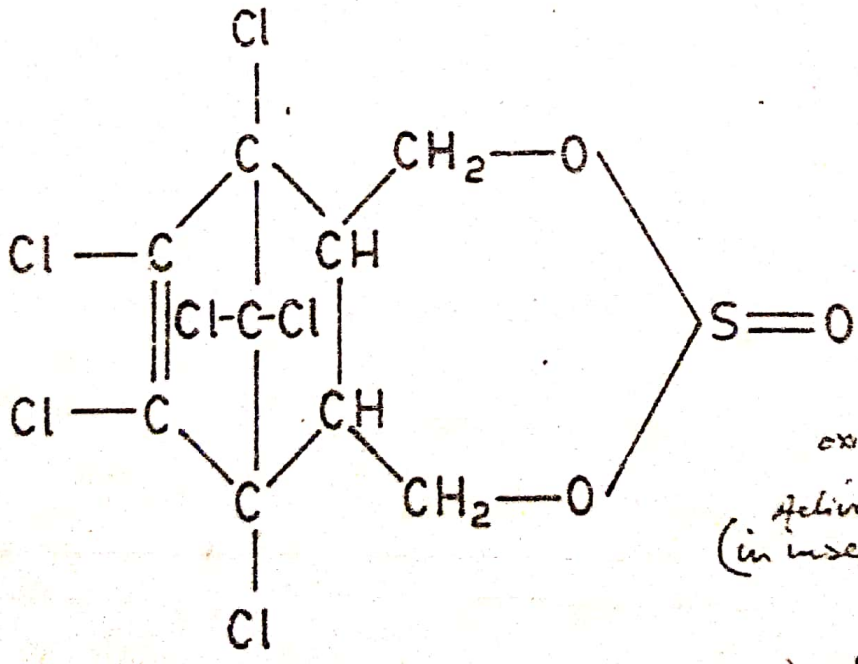
Endo 2x0

Dieldrin

Endrin: $C_{12}H_8Cl_6O$: It is endo-endo isomer of dieldrin differing only in spatial arrangement of two rings. The technical material is light tan powder. It is less stable than dieldrin and easily degraded by heat and light. The pure compound is white crystalline solid with melting point above $200^{\circ}C$. The formulations of endrin are stabilized with hexamethylene tetra-amine. It is amongst the most toxic organochlorine insecticides. It has a surprisingly different spectrum of activity from dieldrin and is used for the control of aphids and lepidopterous larvae. It is readily isomerised in the light to form non-toxic ketone. Like endrin isodrin is also an endo-endo isomer of aldrin. The isodrin is not used in agriculture but is employed for the production of endrin which is the epoxide of isodrin. Isodrin and endrin are similar in their toxic effect.



Endosulfan: C₉H₆Cl₆O₃S : Finkenbrink in the year 1956 described its insecticidal properties. The technical material is brownish crystalline solid with melting point 70-100°C. It is composed of two stereoisomers alpha and beta together with unreacted compound. It is a general purpose insecticide effective against different pests. It is not harmful to bees and natural enemies and has acaricidal properties also.



Endosulfan

