BENZENE HEXACHLORIDE

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Introduction

BHC, benzene hexachloride or 1,2,3,4,5,6-hexachlorocycIohexane, has the empirical formula C6H6 CI6 and was first prepared in 1825 by Michael Faraday, who did not recognize its insecticidal properties.

In 1912, Van der Linden discovered four isomers.

In 1942, Dupire and Raucourt in France and Slade in England both discovered the insecticidal properties of BHe. The British group isolated the toxic y-isomer and named it lindane in honor of Van der Linden.

BHC consists of a mixture of six chemically distinct isomers and heptachlorocycIohexanes and octachlorocycIohexanes.

Crude BHC can be prepared by the chlorination of benzene in the presence of ultraviolet light (Slade, 1945).

It is a grayish or brown amorphous solid with a characteristic musty odor. This odor gives an off-flavor to fruits and potatoes which somewhat limits its agricultural use. Crude BHC begins to melt at 65°e.

The water solubility of crude BHC is in the range of 10-32 ppm.

The toxicity of BHC is proportional to the content of its toxic element, the y-isomer. This isomer, by contact, stomach, or fumigant action, is about 50 10,000 times more effective than the other isomers (Back, 1951; Metcalf, 1947).

It is toxic to mammals, with an acute oral LDso in rats of 125 mg/kg (Sherman, 1948).

Preparations that contain at least 99 % of the y-isomer are called lindane.

Furthermore, the isomers of BHC have different actions. The y- and oc-isomers are stimulants of the central nervous system, with the principal symptom being convulsions. The {3- and b-isomers are depressants of the central nervous system.

There are almost no other chlorinated cyclohexane derivatives which can be used for insecticidal purposes; trichloro-, heptachloro-, octochloro-, and enneachlorobenzenes are practically nontoxic.

Nor are hexamethyland hexaethylcyclohexanes good insecticides.

Cyclodiene Compounds

Cyclodiene compounds are the collective group of synthetic cyclic hydrocarbons consisting of such important insecticides as chlordane, heptachlor, aldrin, dieldrin, and endosulfan. A number of cyclodiene compounds are produced by the Diels-Alder reaction.

Chlordane

Technical chlordane is a dark amber viscous liquid with a cedar-like odor.

It contains approximately 60% chlordane, with the remainder being hexa-, hepta, and nanochlor and other related dicyclopentadiene derivatives.

Chlordane is insoluble in water and soluble in most organic solvents.

It is susceptible to high temperature and alkaline treatments.

It is compatible with most common insecticides. Chlordane has two structural isomers, cis- and trans-octachloromethano- tetrahydroindane (or 13- and IX-chlordane, respectively).

Chlordane is toxic to mammals, with an acute oral LDso in rats of 225-590 mg/kg. It can be absorbed through the skin. trans-Chlordane is sometimes referred to as y-chlordane by the industry.

Heptachlor

The two isomers of chlordane can be separated by chromatographic adsorption on aluminum oxide, and it is then possible to obtain two further derivatives of chlordane-heptachlor and hexachlor.

Heptachlor, a white crystalline solid, is four to five times more insecticidal than technical chlordane and is also more toxic than the f3-isomer of chlordane.

The acute oral LD50 of heptachlor in rats is 90 mg/kg. Heptachlor is stable to heat up to 160°C, light, moisture, air, acids, bases, and oxidizing agents.

The melting point of the pure compound is 95°C, while the technical product has a melting range of 46-74°C.

Heptachlor epoxide is more toxic than heptachlor, so the epoxidation is a vital process to produce toxicity.

The epoxidation of heptachlor cannot be accomplished by simple chemical means, e.g., with peroxy acids, which are known to cause epoxidation of aldrin to dieldrin.

Recently, a chromic acid oxidation method has been found to produce heptachlor epoxide from heptachlor in small quantities.

Aldrin

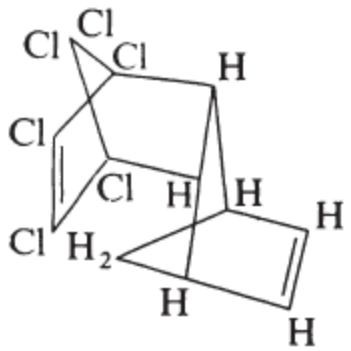
Aldrin, a white crystalline solid with a melting point of 100-103°C, is a residual compound with a vapor pressure of 6 x 10- 6 mm Hg at 25°C.

Aldrin is almost insoluble in water and soluble in most organic solvents. The technical product is a tan to brown solid with a small amount of supernatant liquid at 25°C.

Its setting point is 49-60°C, and it contains approximately 78 % aldrin.

Aldrin is stable to alkali and dilute acid. It is readily converted in plant and animal tissue and in the soil to its epoxide, dieldrin. Hence aldrin shows the same toxic effects as dieldrin.

The spatial configuration of aldrin is:



ALDRIN

Since it is endo-exo, it has the chair formation.

Dieldrin (HEOD)

Dieldrin, which is the epoxy of aldrin, is one of the most persistent chemicals ever known.

It has been used extensively since 1952, especially in situations where a long-lasting residual effect is advantageous.

Dieldrin has a melting point of 173°C, and its vapor pressure is 1.8 x 10- 7 mm Hg at 25°C (less volatile than aldrin).

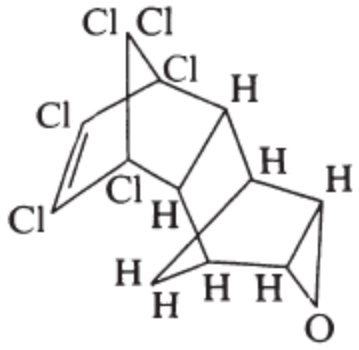
The pure compound is an odorless, white crystalline solid, while technical dieldrin is a flaky tan solid with a setting point of 95°C.

Dieldrin is as insoluble as aldrin in water and less soluble in organic solvents.

Only such procedures as treatments with strong acid or long exposure to intense ultraviolet light are known to decompose dieldrin.

It is less apolar than aldrin. Dieldrin can be absorbed through the skin and it acts as a stimulant of the central nervous system.

The spatial configuration of dieldrin is



DIELDRIN

The toxic activities of aldrin and dieldrin resemble those of fJ-chlordane, heptachlor, and lindane.

Three-dimensional studies of these compounds indicate that certain of the chlorine atoms and methylene groups occupy similar spatial configurations.

Also, houseflies that show resistance to the aldrin, dieldrin, chlordane, heptachlor group also are resistant to lindane.

Toxaphene

It is an economically important insecticide, particularly for cotton.

In 1971, 50 million pounds of toxaphene were produced, accounting for nearly 40% of all the chlorinated hydrocarbon insecticides produced in the United States in that year.

Insecticidal uses of toxaphene have been banned in the United States since 1983.

The first toxic component isolated and identified was Toxicant B, 2,2,5-endo, 6-exo, 8,9,1O-heptachlorobornane.

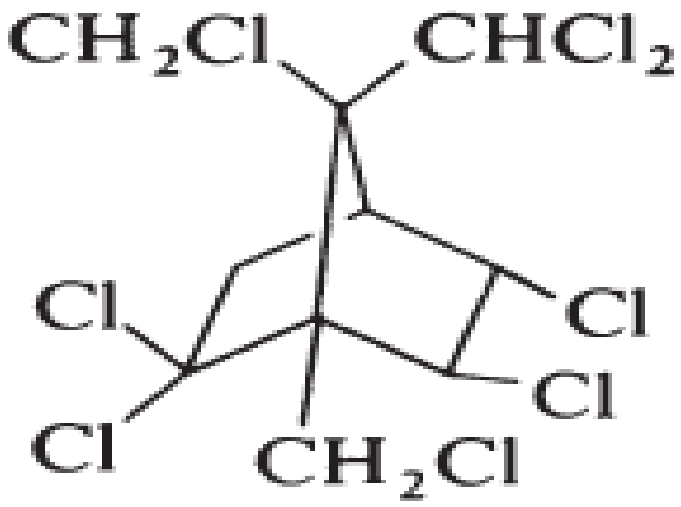
Subsequently the most toxic component, Toxicant A, was simultaneously identified by two groups. It consists of two similar components.

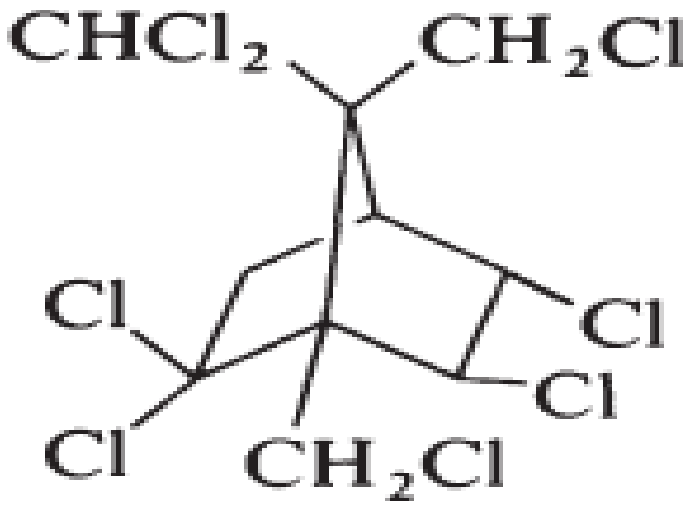
Toxicant C, another toxic component, was isolated and identified by Anagnostopoulos.

Toxaphene is a mixture of isomers with a melting range of 65-70°C.

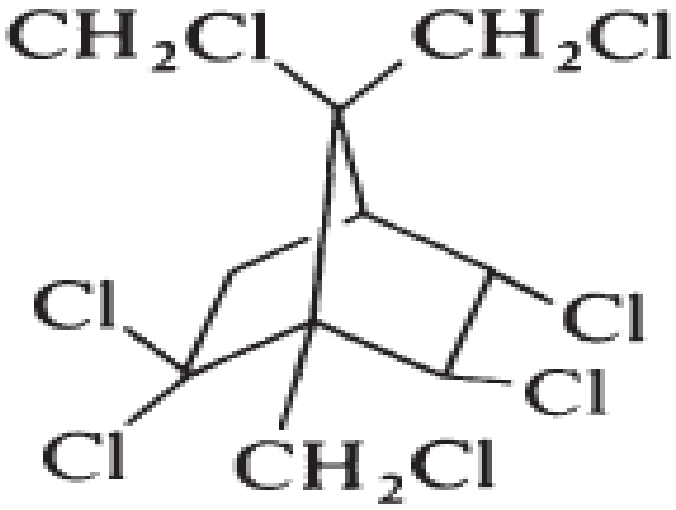
It is a yellow wax and is soluble in most organic solvents and in water at a level of 3 ppm.

Toxaphene is stable except in the presence of alkali, sunlight, or heat above 155°C, all of which cause it to dehydrochlorinate

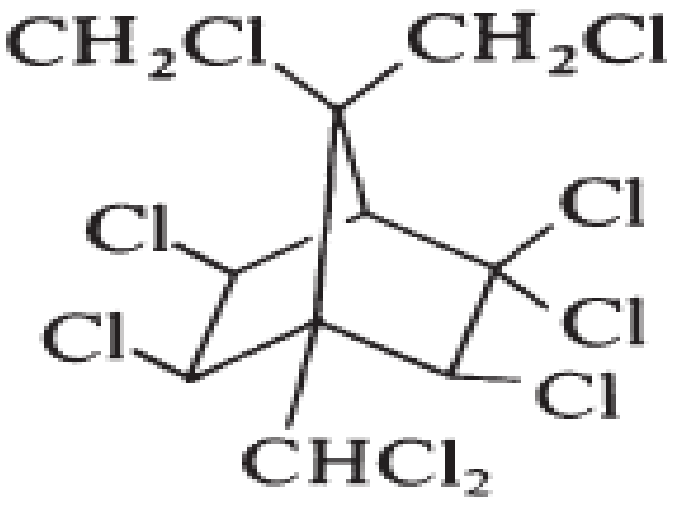




TOXICANT A



TOXICANT B



TOXICANT C

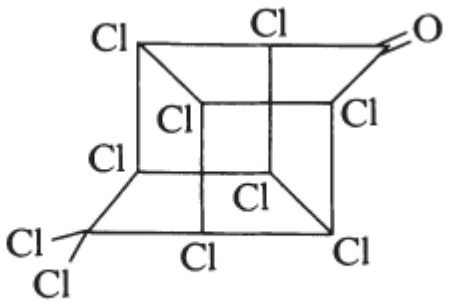
Strobane

A product similar to toxaphene is Strobane, which is prepared by chlorinating camphene and pinene to contain 65% chlorine.

It is called terpene polychlorinate and is a viscous, straw-colored liquid with a mild aromatic odor. Strobane is cheap to produce and has a residue effect.

Kepon

A product similar to mirex is Kepone, which is a white to tan powder relatively soluble in water and some organic solvents. Its structure is

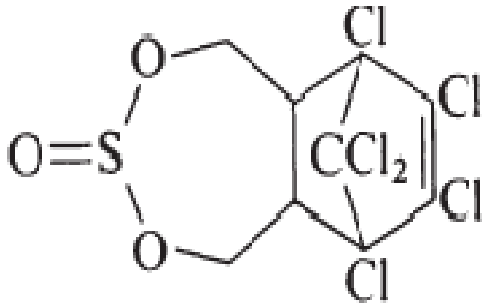


DECACHLOROOCTAHYDRO-1,3,4-METHENO-2*H*-CYCLOBUTA[*c*,*d*]PENTALEN-2-ONE

Kepone is toxic, with an acute oral LD50 in rats of 95 mg/kg, and it is an acaricide in addition to being an insecticide. Both Kepone and mirex are used as stomach poisons in the form of bait, and they control slugs, snails, and fire ants.

Endosulfan

A related insecticide, also an acaricide, is endosulfan. It has the commercial name Thiodan. It is a brownish crystalline solid with a setting point of 70-1 00°c.

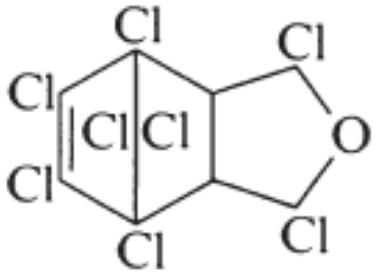


6,7,8,9,10,10-HEXACHLORO-1,5,5a,6,9,9a-HEXAHYDRO-6,9-METHANO-2,4,3-BENZODIOXATHIEPIN 3-OXIDE

Endosulfan is a mixture of two isomers, one with a melting point of 106°C and the other 212°C. It is moderately soluble in most organic solvents and insoluble in water.

Telodrin

Telodrin has been developed as a soil insecticide for corn, alfalfa, clover, etc. It is known to be less stable than aldrin. It is solid, with a melting point of 248-257°C.



1,3,4,5,6,7,8,8-OCTACHLORO-3a,4,7,7a-TETRAHYDRO-4,7-METHANOPHTHALAN

The acute oral LD50 of Telodrin in rats is 4.8 mg/kg; it is readily absorbed through the skin.