Persistent Chlorinated Pesticides

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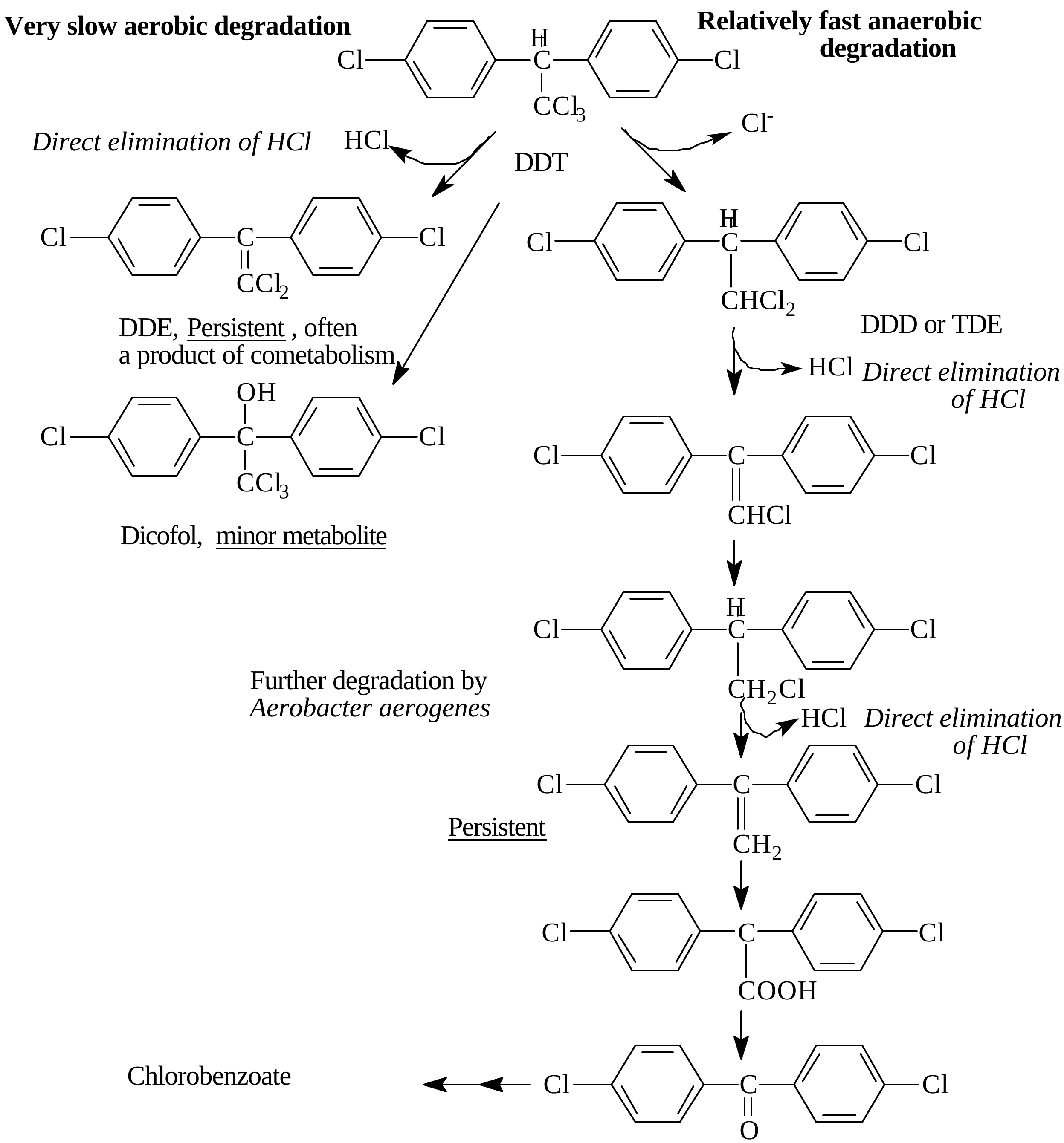
DDT

Persistence of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) and its daughter products in the environment and their effects on bird populations sparked the environmental movement in the early 1960s. Studies at that time showed that DDT and its first dechorination product, DDE, are relatively stable in aerobic environments, but that these compounds partially and slowly degrade in anaerobic environments by a series of dechlorinations and dehydrogenations (direct eliminations of HCl). Numerous metabolites not on the mineralization sequence may also accumulate to a minor degree, for example, dicofol.

The primary presistent product of DDT contamination is DDE, which retains most of the environmental toxicity of DDT. There have been no reports of DDE (or DDT) mineralization by bacteria in pure culture.

Degradation of DDT by *Aerobacter aerogenes* and various marine algae proceeds by direct elimination of HCl between two adjacent carbons with formation of the double bond.(Neilson 1990)



The nonspecific attack on DDT by *Phanerochaete chyrsosporium* is oxidative, resulting in various metabolites, including DDD, dicofol, DDNU (unchlorinated ethylene), and others.

Aerobic degradation of DDT by dioxygenase attack on the ortho and meta positions by *Alcaligenes eutrophus* A5 (Nadeau, Menn et al. 1994). 4-Chlorobenzoate was a stable intermediate of this transformation.

Cometabolism of DDE by biphenyl-degrading *Pseudomonas* strain, producing ring hydroxylation, including products from the cleavage of one ring [Hay, 1998 #15525].

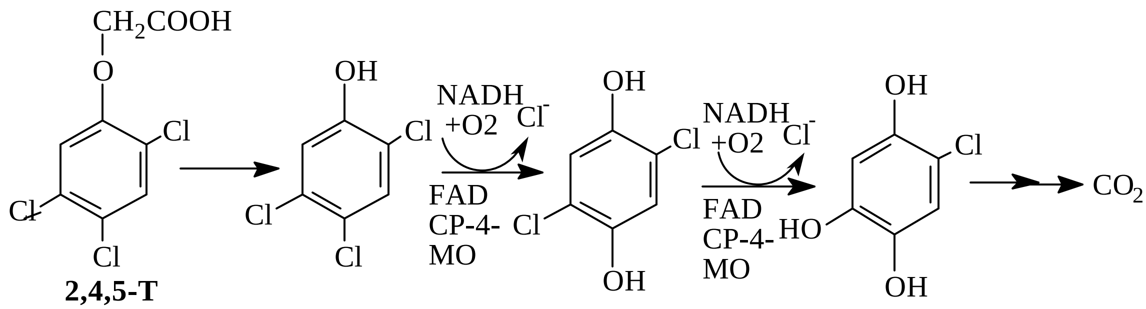
Phenoxyacetates

2,4,5-T — (2,4,5-trichlorophenoxy)acetic acid)

Called agent orange; in use as defoliant in 60s and 70s. Toxicity due to dioxin contamination. No longer used. Persistent in aerobic soils. Dechlorinated anaerobically to 2,4-D; 2,5-D and various monochlorinated phenoxy acetic acids and phenols in anaerobic cultures (Gibson and Suflita 1990).

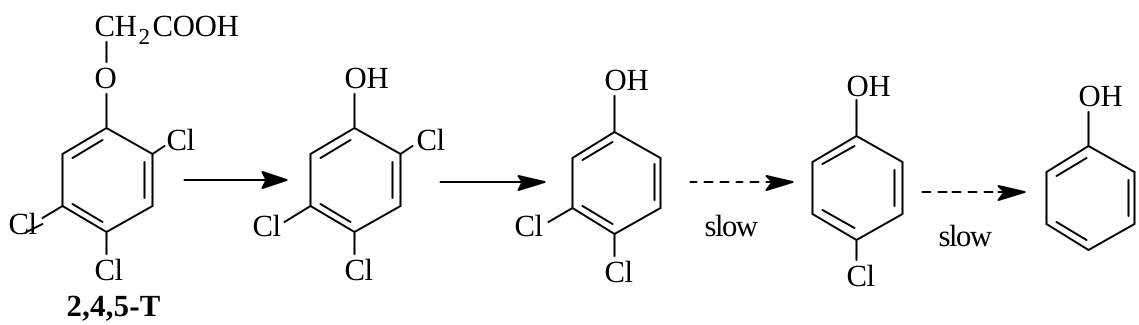
Degradation of 2,4,5-T enhanced at high concentrations using *Burkholderia cepacia* AC1100, which was isolated using 2,4,5-T as sole source of carbon and energy (Kellogg, Chatterjee et al. 1981). "Plasmid-assisted molecular breeding" was used: A continuous culture was inoculated with various bacteria from contaminated sites and with lab strains known to contain plasmids involved in aromatic degradation (e.g. TOL). Starting with low levels of 245T and higher levels of the substrates of the plasmid-coded enzymes, the culture was gradually weaned onto 245T as sole source of carbon and energy. Eventually a single strain was isolated capable of growth on 245T (Kilbane, Chatterjee et al. 1982).

Pathway proceeds through 2,4,5-trichlorophenol, then by hydroxydechlorination of the para chlorines [Xun, 1996 #15526] by action of a flavin adenine dinucleotide (FAD) containing chlorophenol 4-monooxygenase, leading to complete mineralization of the chlorophenol.



Mineralization by AC1100

Anaerobic degradation similar to 2,4-D: cleavage of phenoxy-ether link, then dechlorination, usually, ortho, meta, and para:



2,4-D, (2,4-dichlorophenoxy)acetic acid

<u>Not persistent</u>. Still widely used as a selective broad-leaf herbicide. 2,4-D is attacked as a growth substrate by various bacterial genera: *Pseudomonas, Achromobacter, Flavobacteria, Coynebacteria, Arthrobacteria*..

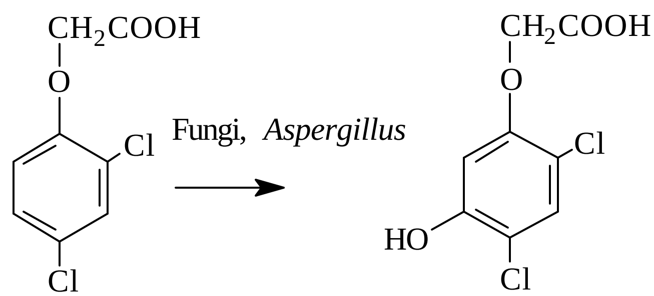
Fungal degradation is incomplete with monooxygenase attack and hydroxylation of the ring.

Aerobic acterial degradation by

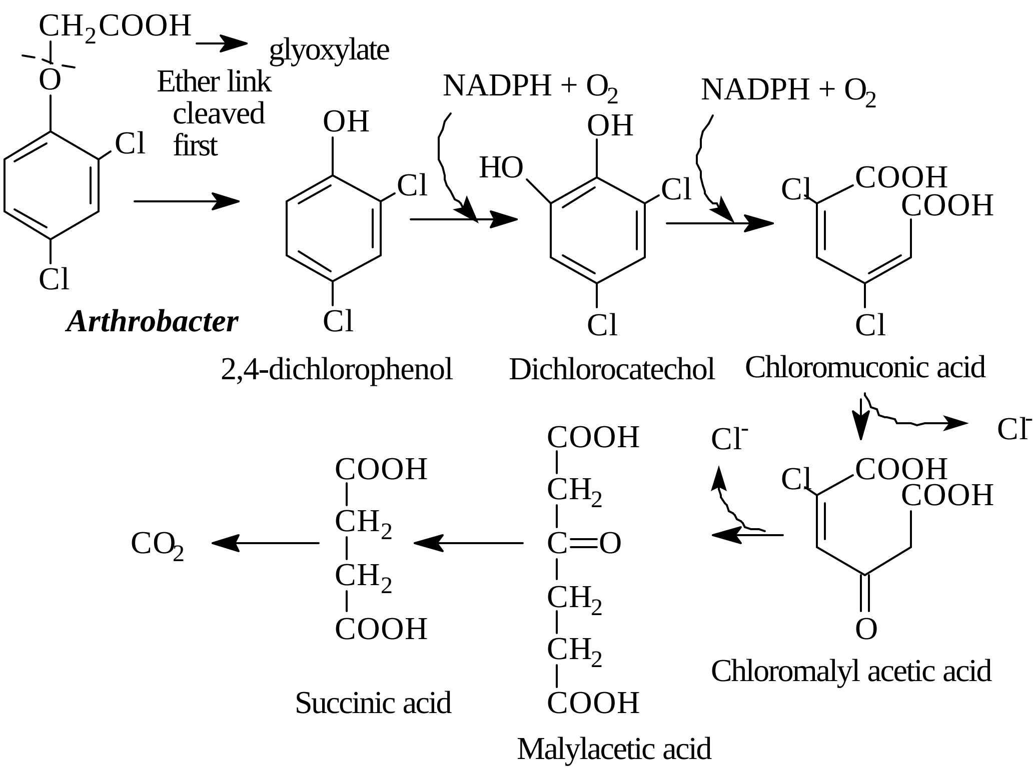
1) Simultaneous ring hydroxylation and cleavage of 2-carbon substituent at the ether linkage, followed by

2) ring cleavage, 3) dehalogenation, 4) β-oxidation of long aliphatic acid residue

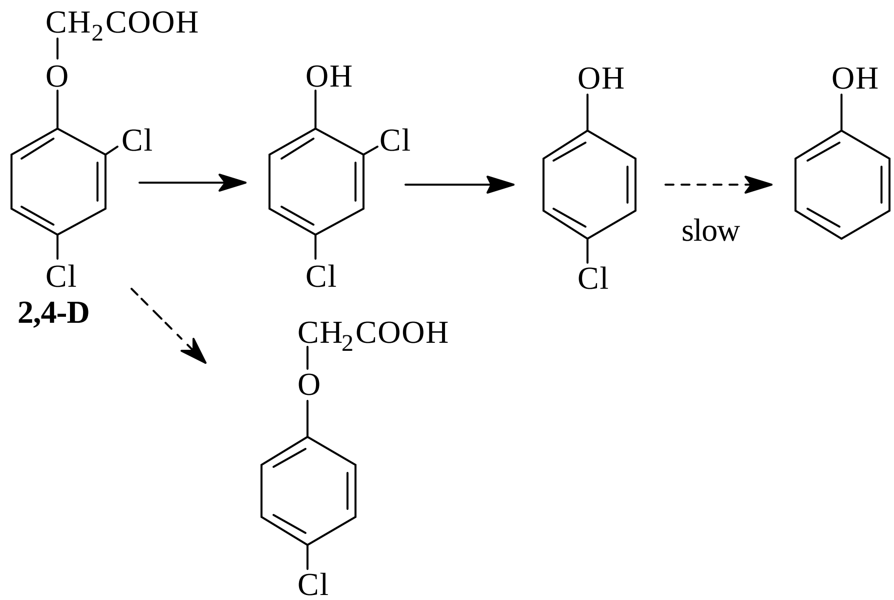
Phenoxyalkanoic acids degrade through formation of catechols then ring opening and formation of muconic acid. This is an aerobic process requiring oxygen and NADPH for the formation of the catechol and the ring cleavage.



2,4-D

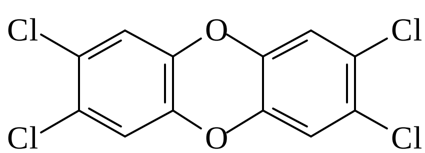


Anaerobic degradation of 2,4-D to 2,4-dichlorophenol then to 4-chlorophenol, rapid, then slowly dechlorinated and mineralized. Some formation of 4-chlorophenoxyacetate.



Dioxin

TCDD, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, is the toxic form.



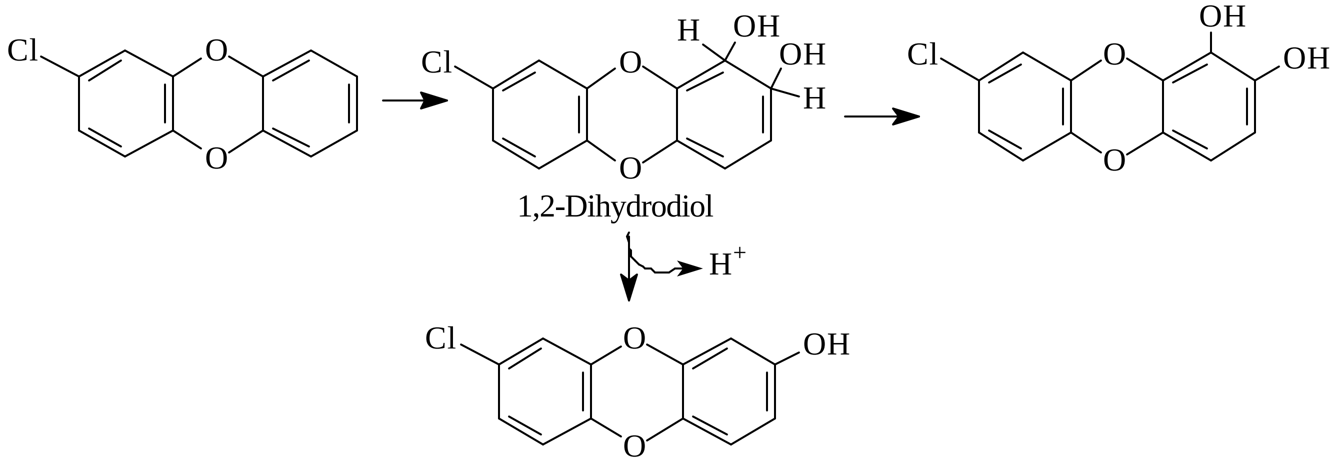
Sometimes in high concentration in heavily contaminated sites: Times beach MO, >100 mg/kg; Seveso Italy, = 3000 mg/kg; Agent orange = 1-47 mg/L TCDD (byproduct of 2,4,5-trichlorophenol production). Combustion of chlorine containing plastics leads to widespread low levels in the environment starting in 1940. Low acute toxicity, chloracne in humans. No significant human toxicity risks found at Times Beach. Teratogenic effects in animals (Mus), but no reproductive abnormalities in Times Beach. High-risk human carcinogen, soft tissue sarcoma; not confirmed in Times Beach.

Various aerobic bacteria and fungi have been reported to partially oxidize TCDD, including *Pseudomonas pudita*, *Trichoderma viride*, *Bacillus megaterium* and *Nocardiopsis* (Arthur and Frea 1989).

Oxidation by ligninolytic white-rot fungus, *Phanerochaete chrysosporium*. Radiolabeled TCDD degraded to $^{14}CO_2$, 2% in 30d (Bumpus, Tien et al. 1985).

Little loss of TCDD is seen after long term (2 yr) incubation in soils.

Biodegradation pathways both aerobic and anaerobic, but slow. Anaerobic dechlorination [Barkovskii, 1996 #15527] and some nonspecific hydroxylation. 2-Chloro-benzo-*p*-dioxin is hydroxylated by *Alcaligenes* strain JB1, a strain that grows on biphenyl (Parsons and Storms 1989):



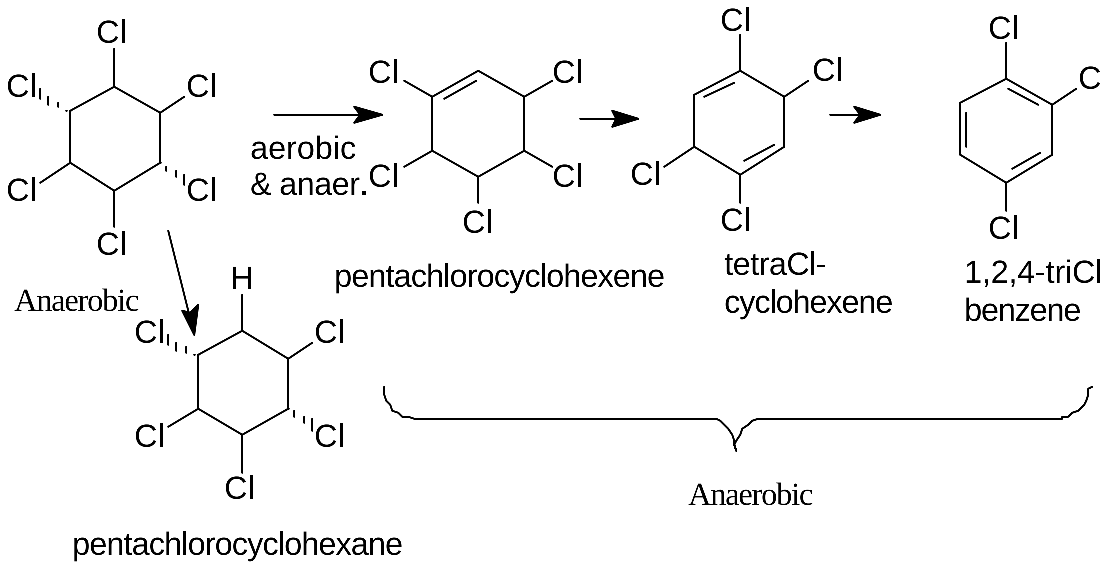
This dioxygenase activity is cometabolic in benzoate and methylbenzoate-fed cultures. 1,3-, 2,7-, and 2,8-dichloro and 2,2,4-trichlorodibenzo-*p*-dioxins are also cometabolized, but slowly. No degradation of tetrachlorodibenzo-*p*-dioxin.

Lindane

γ-hexachlorocyclohexane, γHCH. Only γ is insecticidal.

Dehydrochlorination to pentachlorocyclohexene carried out by *Bacillus cereus*.

Anaerobic dechlorination to γ-3,4,5,6-tetrachlorocyclohexane in flooded soils, followed by further dechlorination and reduction of the ring over several weeks.

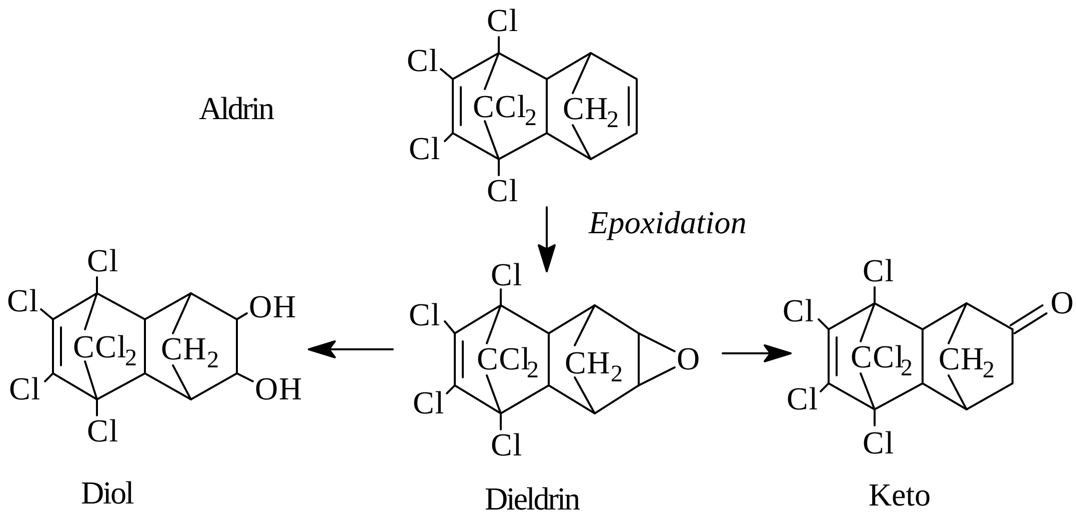


Clostridium rectum use lindane as an electron acceptor in the Stickland reaction leading to ATP production (normally using amino acids such as leucine, glycine as e acceptors) (Ohisa and Kurihara 1982). The metabolites are γ-1,2,3,4,5,6-hexachlorocyclohexene, γ-1,3,4,5,6-pentachlorocyclohexene, 1,2,4-trichlorobenzene and 1,4-dichlorobenzene. ATP synthesis was indicated by luciferase-luciferin reaction and phosphorylation of ^{32}P-labeled phosphate.

Chlorinated cyclodiene insectides

Aldrin & Dieldrin

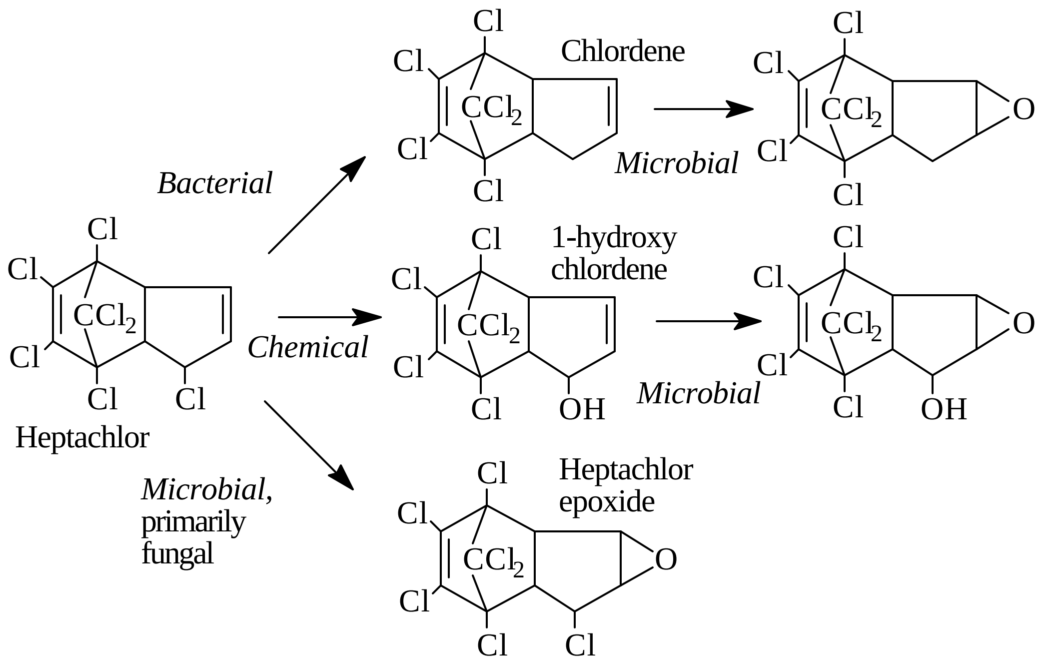
Aerobically, various *Aspergillus niger*, *A. flavus*, *Penicillium notatum* convert aldrin to dieldrin by a monooxygenation to an epoxide. Dieldrin is very stable, slowly oxidizing to a diol or to keto-aldrin (Khan 1980).



Under anaerobic conditions, such as in sewage sludge digesters, dieldrin is slowly degraded, ca. 26% after a lag period of 75d (Battersby and Wilson 1989), Anaerobic degradation of aldrin and dieldrin proceeds by mono or di-dechlorination, with the epoxides being less reactive than parent compound (Baxter 1990). Usually dechlorination is of CCl_2 similar to DDD (Mohn and Tiedje 1992).

Heptachlor

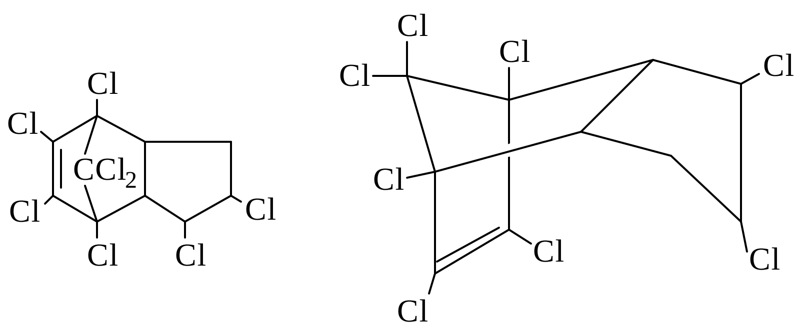
The aerobic attack on heptachlor is similar, a stable epoxide is formed, sometimes following initial chemical hydrolysis or dechlorination. This sequence is observed in soils and with various pure cultures, including *Rhizopus, Fusarium, Penicillium, Trichoderma, Nocardia, Streptomyes, Bacillus,* and *Micromonospora.*



Limited reductive dechlorination of the alkyl CCl_2 occurs in anaerobic environments, resulting in persistent, partially degraded products (Mohn and Tiedje 1992).

Chlordane

Insecticide used to protect against termites. Persistent.



Chlordane

Degraded by soil actinomycete, *Nocardiopsis*, including *cis* and *trans* isomers (MacRae 1989). Products include dichlorochlordene, oxychlordene, heptachlor-epoxide, chlordene chlorohydrin, and 3-hydroxy -*trans*-chlordane (Beeman and Matsumura 1981). Degraded at least partially in aerobic sewage treatment, 60-90% lost (Sabatini, Smith et al. 1990)

References

Arthur, M. F. and J. I. Frea (1989). "2,3,7,8-Tetrachlorodibenzo-p-dioxin: Aspects of its important properties and its potential biodegradation in soils." J. Environ. Qual. **18**: 1-11.

Battersby, N. S. and V. Wilson (1989). "Survey of the anaerobic biodegradation potential of organic chemicals in digesting sludge." Appl. Environ. Microbiol. **55**: 433-439.

Baxter, R. M. (1990). "Reductive dechlorination of certain chlorinated organic compounds by reduced hematin compared with their behaviour in the environment." Chemosphere **21**: 451-458.

Beeman, R. W. and F. Matsumura (1981). "Metabolism of *cis*- and *trans*-chlordane by a soil microorganism." J. Agric. Food Chem. **29**: 84-88.

Bumpus, J. A., M. Tien, D. Wright and S. D. Aust (1985). "Oxidation of persistent environmental pollutants by a white rot fungus." Science **228**: 1434-1436.

Gibson, S. A. and J. M. Suflita (1990). "Anaerobic biodegradation of 2,4,5-trichlorophenoxyacetic acid in samples from a methanogenic aquifer - stimulation by short-chain organic acids and alcohols." Applied and Environmental Microbiology **56**: 1825-1832.

Kellogg, S. T., D. K. Chatterjee and A. M. Chakrabarty (1981). "Plasmid-assisted molecular breeding: new technique for enhanced biodegradation of persistent toxic chemicals." Science **214**: 1133-1135.

Khan, S. U. (1980). Pesticides in the Soil Environment. Pesticides in the Soil Environment. Amsterdam, Elsevier Scientific Publ. Co.

Kilbane, J. J., D. K. Chatterjee, J. S. Karns, S. T. Kellogg and A. M. Chakrabarty (1982). "Biodegradation of 2,4,5-trichlorophenoxyacetic acid by a pure culture of Pseudomonas cepacia." Appl. Environ. Microbiol. **44**: 72-78.

MacRae, I. C. (1989). "Microbial metabolism of pesticides and structurally related compounds." Reviews of Environmental Contamination and Toxicology **109**: 1-87.

Mohn, W. W. and J. M. Tiedje (1992). "Microbial Reductive Dehalogenation." Microbiol Rev **56**(3): 482-507.

Nadeau, L. J., F. M. Menn, A. Breen and G. S. Sayler (1994). "Aerobic degradation of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) by Alcaligenes eutrophus A5." Applied and Environmental Microbiology **60**(1): 51-55.

Neilson, A. H. (1990). "The biodegradation of halogenated organic compounds - a review." Journal of Applied Bacteriology **69**: 445-470.

Ohisa, N. and N. Kurihara (1982). "ATP synthesis associated with the conversion of hexachlorocyclohexane related compounds." Arch Microbiol **131**: 330-333.

Parsons, J. R. and M. C. M. Storms (1989). "Biodegradation of chlorinated dibenzo-para-dioxins in batch and continuous cultures of strain JB1." Chemosphere **19**: 1297-1308.

Sabatini, D. A., J. W. Smith and L. W. Moore (1990). "Treatment of chlordane-contaminated water by the activated rotating biological contactor." Journal of Environmental Quality **19**: 334-338.