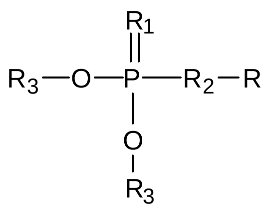
Organophosphorus Pesticides

Stuart Strand

Organophosphorus

Most organophosphorus pesticides are vinyl ester derivatives of phosphates.



R_1 = S or O

R_2 = N, S or O

R_3 = methyl or ethyl substituents

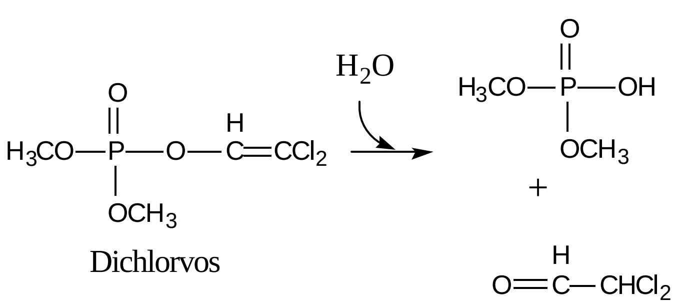
R = various aliphatic & aromatic structures

Four classes of organophosphorus pesticides in use:
Phosphates (R_1, R_2 = O), phosphorothioates (R_1 = S, R_2 = 0), phosphorothiolothionates (R_1, R_2 = S), and phosphonates (with a P-C bond)

Phosphates

Dichlorvos

Dichlorvos is a widely used household insecticide. Degraded by *Pseudomonas melophthora, Bacillus subtilis* and other bacteria. A likely degradative pathway is shown below.

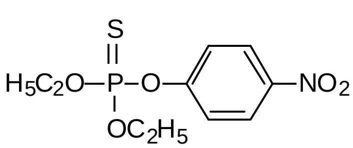


Phosphorothioates

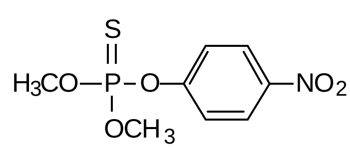
Insecticides, hydrolytically stable in aqueous solutions, biodegradable at various rates.

Parathion

Parathion is highly toxic, used as an insecticide and acaricide.



Parathion



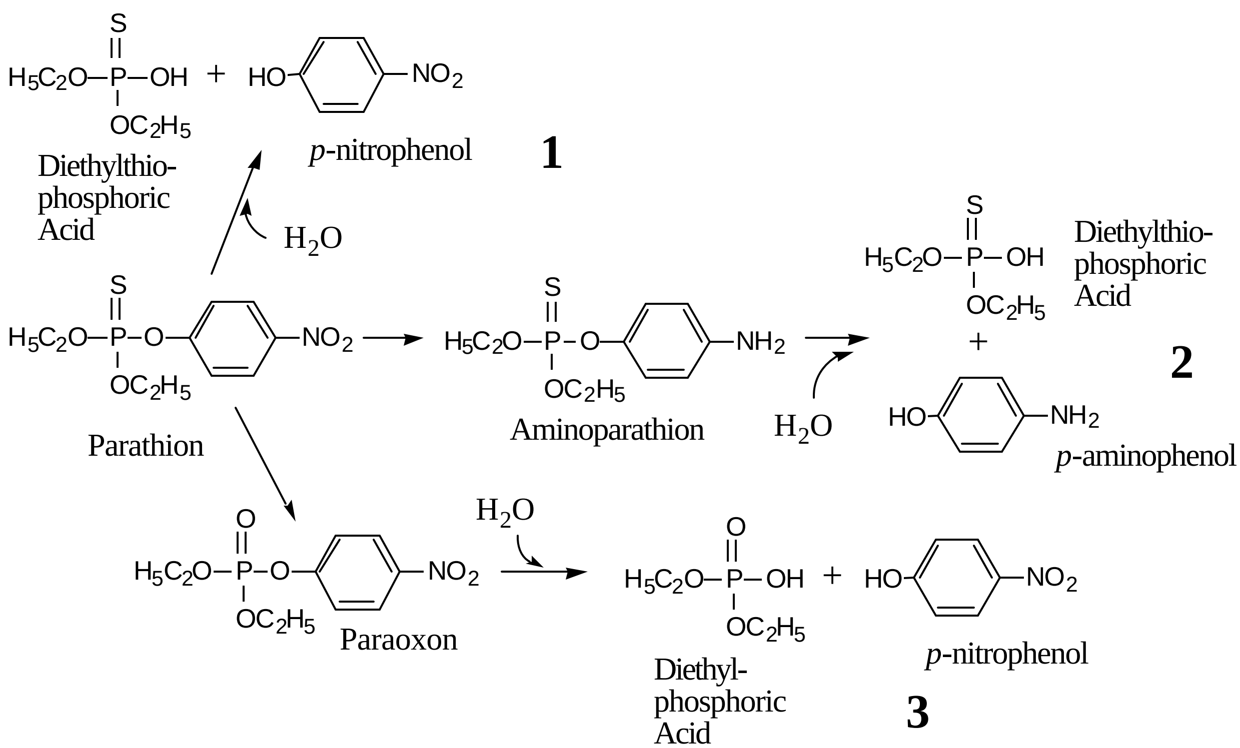
Methyl Parathion

Parathion is degraded in soils and water by three pathways, all of which require acclimatization for complete expression:

1. Hydrolysis to *p*-nitrophenol and diethylthiophosphoric acid. Usual in aerobic soils. *p*-Nitrophenol is often degraded by reduction to *p*-aminophenol.

2. Reduction to aminoparathion, which is then hydrolyzed to *p*-aminophenol and diethylthiophosphoric acid under low oxygen levels (microaerophilic). Usual in anaerobic environments

3. Small amounts of oxidation to paraoxon. This is the main mammalian metabolic pathway. Paraxon is further degraded to nitrophenol and diethyl phosphoric acid in the environment.



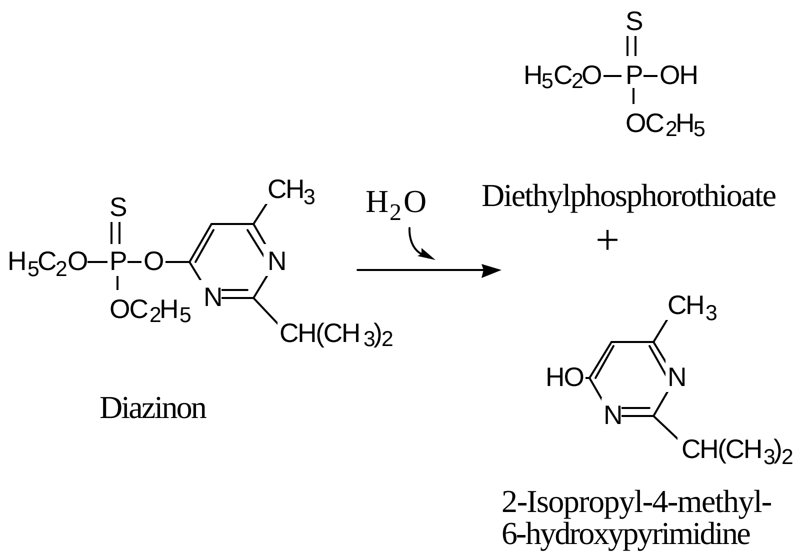
The *p*-nitrophenol is metabolized aerobically by monooxygenation ortho to the hydroxyl, followed by loss of the nitroso group and cleavage of the catechol. Alternately, the nitroso group is cleaved by an oxygenase attack forming hydroquinone, which is further hydroxylated and cleaved. *p*-Nitrophenol also degrades in flooded soils with the release of NO_2^- and CO_2. Parathion is degraded by a bacterium, *Flavobacterium* sp, an algae *Chlorella pyrenoidosa*, and a fungus *Penicillium waksmani*. Degradation occurs in aerobic and flooded (anaerobic soils), often involving consortia. Thus *Flavobacterium* is unable to use *p*-nitrophenol which is degraded by other bacteria. However a *Pseudomonas* sp hydrolyzes parathion and degrades the *p*-nitrophenol by reducing it to aminophenol and an *Arthrobacter* sp was able to use parathion or *p*-nitrophenol as sole sources of carbon and energy [1].

Methyl parathion degrades more rapidly (half life 1.2d in estuarine sediments) than parathion, but through similar pathways to those of parathion.

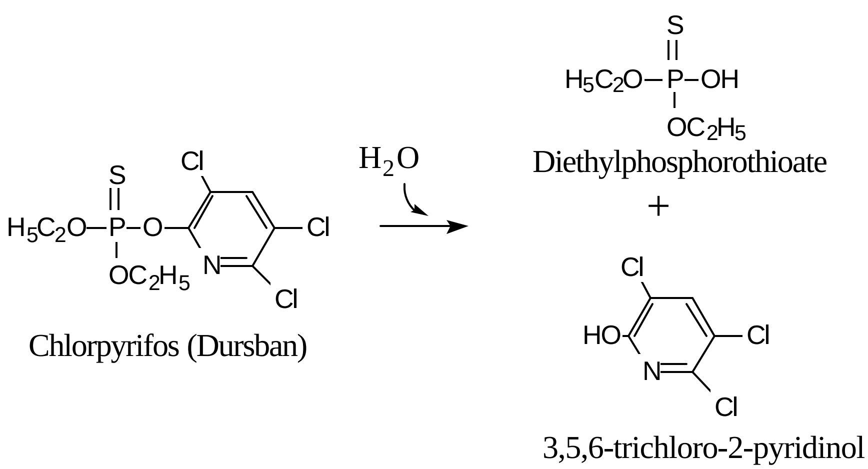
Diazinon

Diazinon is degraded relatively rapidly in acclimated soils. Diazinon-degrading *Flavobacterium* sp. and *Pseudomona aeruginosa* have been isolated.

Diazinon is hydrolyzed to diethyl phosphorothioate and 2-isopropyl-4-methyl-6-hydroxypyrimidine, leading to complete mineralization, often requiring consortia [2].

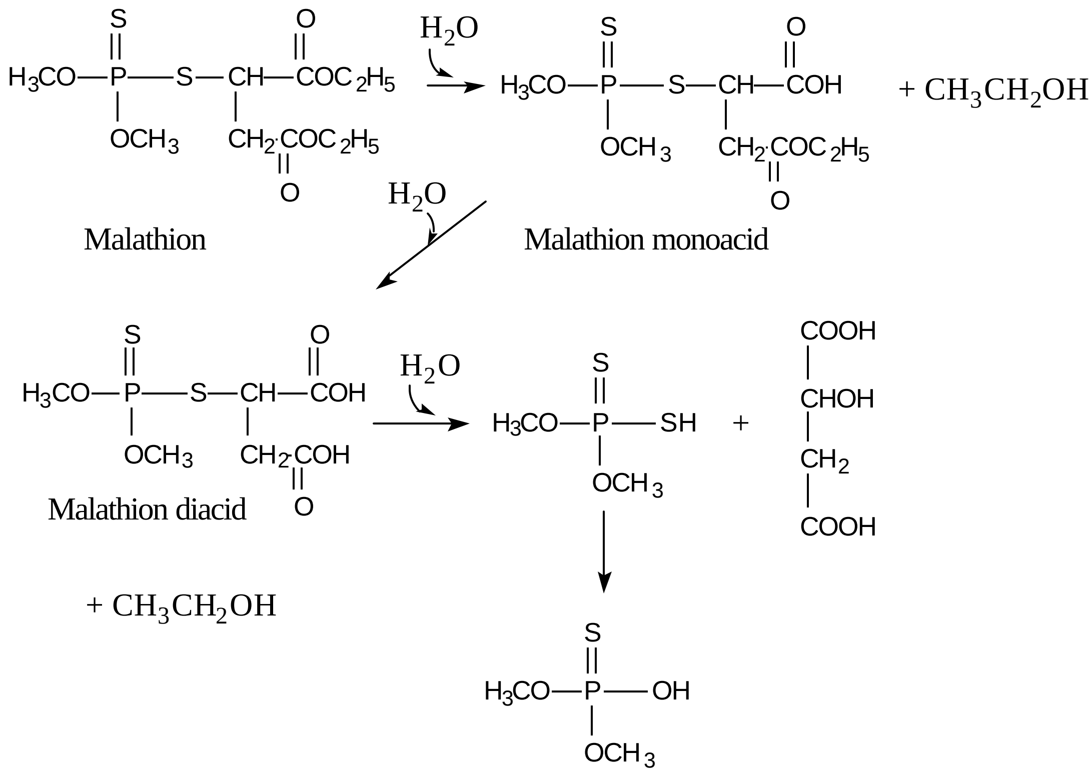


Chlorpyrifos (e.g., Dursban) degraded rapidly (half life of 4-12 weeks in soil and sediment) to 3,5,6-trichloro-2-pyridinol



Phosphorothiolothionates (phosphorodithioates)
These are widely used insecticides

Malathion
Rapidly degraded by a soil fungus *Trichoderma viride* and bacteria, *Pseudomonas* and *Arthrobacter* spp. Attack requires deethylation of the R group side chains before hydrolysis of the phosphorodithionate:

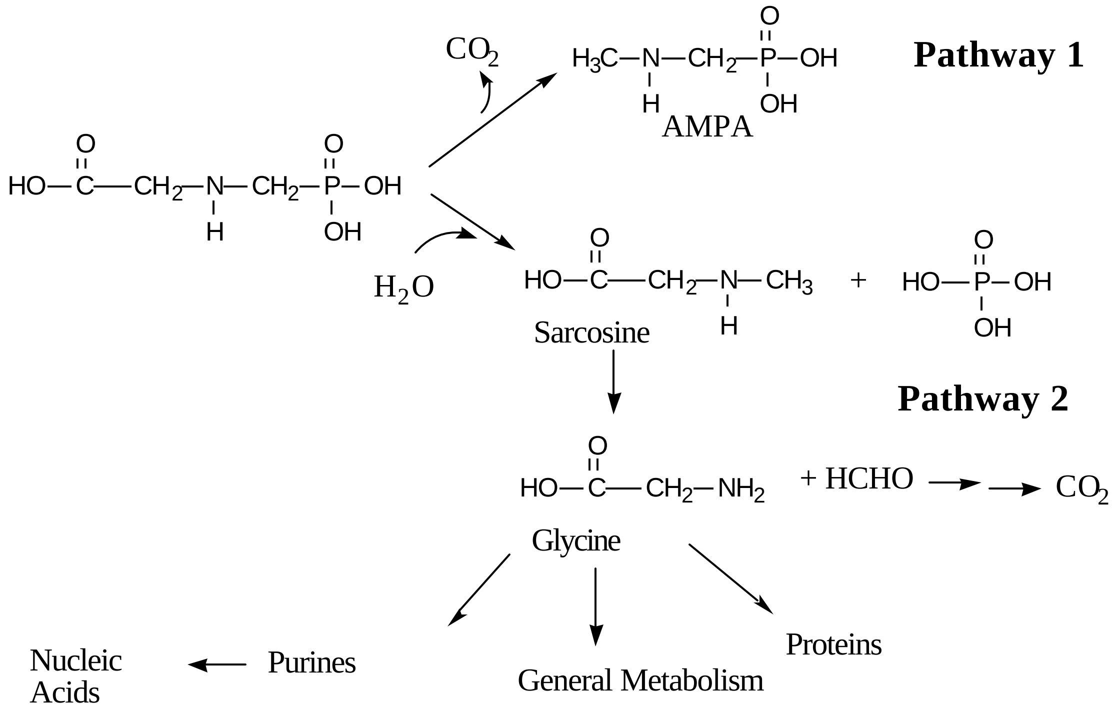


Phosphonates
These compounds have the biologically unusual C-P bond.

Glyphosate
Roundup, *N*-phosphonomethyl glycine. Most important phosphorus-based, broad band herbicide.

The **phosphonates**, including glyphosate, differ from the other organophosphorus pesticides by having a **P-C bond** rather than the ester, P-O-C. The phosponate P is reduced compared to the phosphates.
Glyphosate is rapidly degraded in soils. N methyl amino methyl phosphonic acid (AMPA) has been detected in some soils as the only significant metabolite [3].

Complete degradation goes through glycine and sarcosine with an oxidation of the phosphonate to phosphate.



Same metabolites for aerobic & anaerobic degradation.

Glyphosate can be used as a sole nitrogen source (thorugh glycine).

Degradation of glyphosate by various bacterial species, yielding phosphate through **oxidation** of phosphonate moiety and using phosphate as sole source of P [4]. Some *Alcaligenes* spp stop with phosphate and sacrosine, using only the phosphorus and not the carbon if other carbon sources available [5]. A *Flavobacterium* sp from a sewage treatment plant does the same even in the presence of inorganic phosphate [6]. With other strains the presence of inorganic phosphate in the media may supress the oxidation of glyphosate.

Summary:

- Hydrolysis of P-O-C linkage for phosphorothionates
- Initial modification of R substituent, then hydrolysis of P-S-C linkage for phosphorodithionates
- Oxidation of phosphonates.

References

1. MacRae, I.C., *Microbial metabolism of pesticides and structurally related compounds.* Reviews of Environmental Contamination and Toxicology, 1989. **109**: p. 1-87.
2. Konrad, J.G., D.E. Armstrong, and G. Chesters, Agron. J., 1967. **59**: p. 591-594.
3. Rueppel, M.L., *et al.*, *Metabolism and degradation of glyphosate in soil and water.* J. Agric. Food Chem., 1977. **25**: p. 517-528.
4. Kishore, G.M. and G.S. Jacob, *Degradation of glyphosate by Pseudomonas sp. PG2982 via a sarcosine intermediate.* J. Biol. Chem., 1987. **262**: p. 12164-12168.
5. Lerbs, W., M. Stock, and B. Parthier, *Physiological aspects of glyphosate degradation in Alcaligenes spec. strain GL.* Arch. Microbiol., 1990. **153**: p. 146-150.

6. Balthazor, T.M. and L.E. Hallas, *Glyphosate-degrading microorganisms from industrial activated sludge.* Applied and Environmental Microbiology, 1986. **51**: p. 432-434.

Reviews:
Aislabie, J. and G. Lloyd-Jones, *A review of bacterial degradation of pesticides.* Australian Journal of Soil Research, 1995. **33**(6): p. 925-942.
Khan, S.U., *Pesticides in the Soil Environment*, in *Pesticides in the Soil Environment*. 1980, Elsevier Scientific Publ. Co.: Amsterdam.