ORGANOPHOSPHORUS INSECTICIDES

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Introduction

The OP group of insecticides includes such generally toxic compounds as parathion and TEPP and such selective compounds as malathion and ronnel.

The OP insecticides are used as stomach and contact poisons, as fumigants, and as systemic insecticides for nearly every type of insect control.

Because the number of currently used organophosphorus insecticides is so large, description of their chemical properties will be restricted here to a few important ones that represent groups (or types) of OP compounds.

TEPP (TEPP)

Tepp or TEPP, a pyrophosphate, was the first widely marketed organophosphate insecticide (in 1944).

It was synthesized by Clermont (1854), but apparently nothing was known of its toxic properties until Schrader in 1942 prepared this compound as a nicotinic substance.

Schrader described it as hexaethyltetraphosphate (HETP), but now the main insecticidal component is known to be tetraethylpyrophosphate (TEPP) (Schrader, 1942).

The commercial preparation of HETP contains 10-20% TEPP. When a product contains 40 % or more tetraethylpyrophosphate, it is called tepp.

Tepp is a colorless, hydroscopic liquid, miscible with water but rapidly hydrolyzed to nontoxic diethylphosphoric acid. It is miscible with organic solvents and with aromatic oils but not with kerosene or paraffin.

It is not a systemic insecticide and is too toxic to be on the market today. The hydrolysis of TEPP accounts for its decomposition in sprays and in residues exposed to moisture.

Tepp should therefore be stored in moisture-proof glass, stainless steel, or nickel containers. Its vapor pressure is on the order of 10- 4 mm Hg.

Schradan

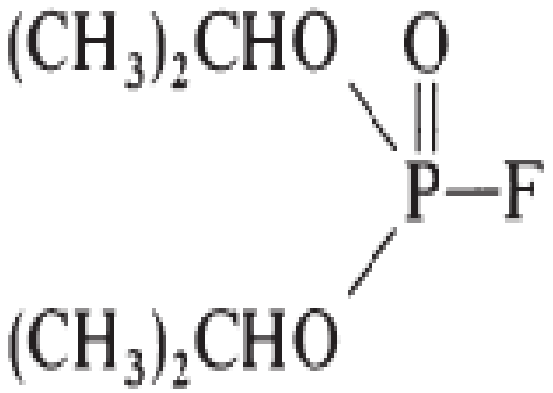
A pyrophosphate safe enough to use as a systemic insecticide is schradan or OMPA (for octamethylpyrophosphoramidate).

Schradan is of historical interest since it was the first OP compound to be studied as a systemic insecticide. Thus it kiIls sucking insects without killing their predators. Since systemic insecticides are polar, they do not penetrate the insect cuticle, which is permeable only to apolar compounds.

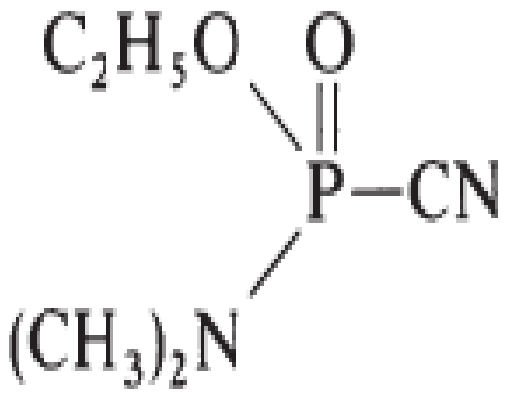
Schradan is a colorless, odorless liquid that is miscible with water and most organic solvents except petroleum hydrocarbons. Its boiling point is 118-122°C at 0.3 mm Hg, and its melting point is 20°C. It has a relatively high vapor pressure, 10- 3 mm Hg at 20°C. It is stable in water.

Phosphorohalides and Cyanides

Phosphorohalides and cyanides are mostly known as "nerve gases,“ since they were first developed as chemical warfare agents and used in the form of mists at low concentrations.



DFP



TABUN

Dimefox

Dimefox has a high vapor hazard (vapor pressure is 0.01 mm Hg at 20°C and 0.4 mm Hg at 30°C) and is more toxic to mammals than to insects.

It is a colorless liquid with a boiling point of 67°C at 4 mm Hg.

Dimefox is an inexpensive systemic insecticide and is highly soluble in water and acts as a powerful anticholinesterase.

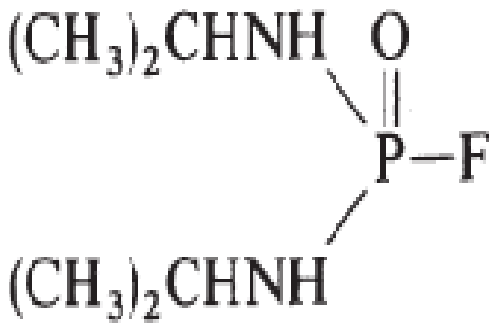
Its practical application should be limited to trunk or soil implantations. Dimefox is also called Pestox 14.

Methylparathion

A similar compound to dimefox is mipafox, which is also called Isopestox or Pestox 15.

It is less volatile (on the order of 10-3 mm Hg at 25°C) than dimefox.

It is a white crystalline solid (melting point 60°C) and is slightly soluble in water (8%).



N,N'-DIISOPROPYLDIAMIDOPHOSPHORYL FLUORIDE

Dialkylarylphosphates Phosphorothioates and Phosphorodithioates

Phosphorothioates or -dithioates are converted to corresponding phosphates or phosphorothioates in the animal or plant tissues and then become much more toxic ("'activation").

Most of the following insecticides are marketed as the phosphorothioate (P=S) and are converted in the animal body to the phosphate (P=O), which is a more potent anticholinesterase.

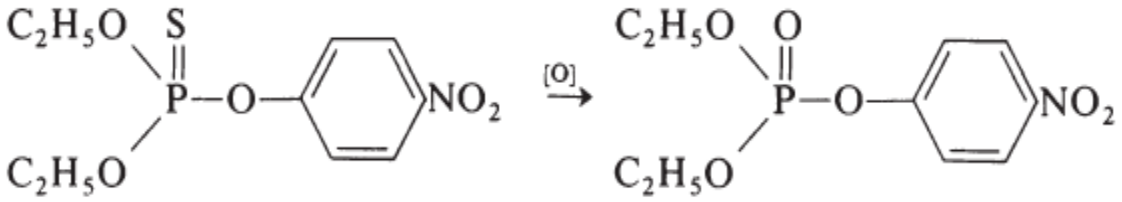
Generally speaking, the p=o analogues are less stable than P=S analogues and are susceptible to hydrolysis.

Also, the P=O analogues may not penetrate well into the insect cuticle, which is more resistant to polar compounds (like phosphates) than to apolar analogues (P=S analogues are less polar than their P=O counterparts).

For instance, paraoxon, a phosphate, is not a good mosquito larvicide; but parathion, a phosphorothioate, is, even though parathion is later converted to paraoxon in the insect's body.

Parathion

The oxidation of parathion to paraoxon is a typical example of in vivo activation:



PARATHION
O,*O*-DIETHYL *O*-*p*-NITROPHENYL
PHOSPHOROTHIOATE

PARAOXON
O,*O*-DIETHYL *O*-*p*-NITROPHENYL
PHOSPHATE

Parathion is highly toxic to mammals, and its use has largely been superseded by less hazardous phosphates such as methylparathion and fenitrothion.

Parathion controls a variety of insects such as aphids, mites, beetles, Lepidoptera, leaf hoppers, leafminers, and other pests found on fruits, cotton, vegetables, and forage crops. It also controls several soil insects such as wireworms, rootworms, and symphilids.

Pure parathion is a colorless, almost odorless liquid, while the technical product is a dark brown liquid with a garlic odor.

It is partially soluble in water and is completely miscible with a variety of alcohols, esters, ethers, and aromatic hydrocarbons.

It is slowly hydrolyzed in water to form p-nitrophenol and diethyl orthothiophosphoric acid.

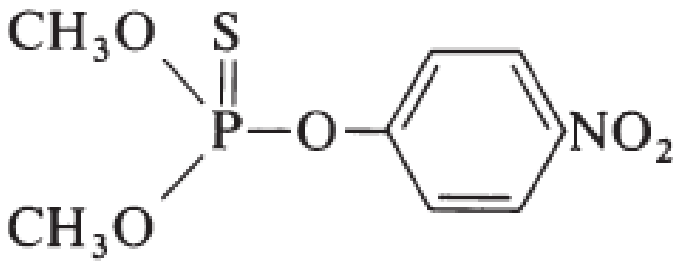
The time for 50 % hydrolysis is 120 days, but this occurs more rapidly in alkaline solution.

Thus parathion has a short residual life that is even shorter under alkaline conditions. It is not affected by oxygen or ultraviolet.

Methylparathion

Methylparathion is simply a dimethyl analogue of parathion. Its selectiveness appears to come from its relatively low dermal toxicity to mammals.

It has the same toxicity to insects as parathion and generally controls the same group of insects. Methylparathion is a white crystalline compound with a melting point of 35-36°C.

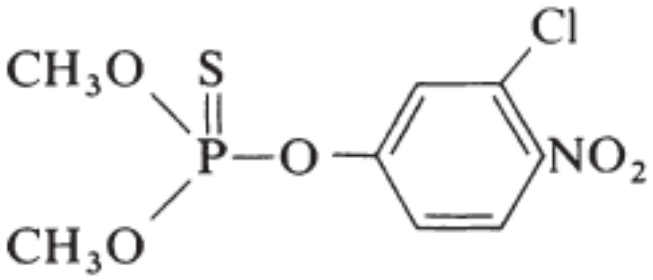


O,*O*-DIMETHYL *O*-*p*-NITROPHENYL PHOSPHOROTHIOATE

- The technical product is an amber liquid.
- Methylparathion is somewhat less stable than parathion, for it hydrolyzes more rapidly in alkali.
- Its volatility is similar to that of parathion (1 x 10- 5 mm Hg at 20°C).
- It was the number one organophosphate insecticide produced in the United States in 1971.

Chlorthion

Chlorthion is also known as Bayer 22/190.

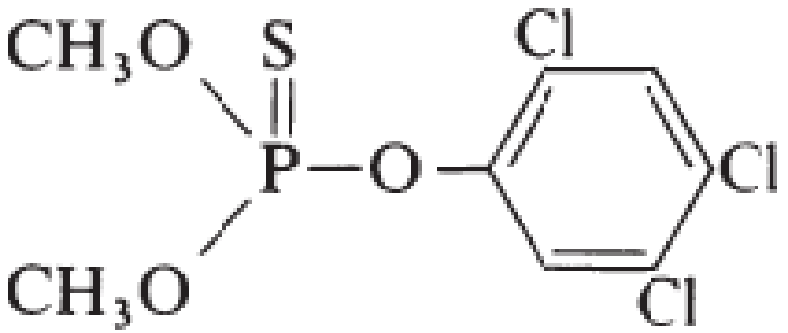


O,*O*-DIMETHYL *O*-3-CHLORO-4-NITROPHENYL PHOSPHOROTHIOATE

Chlorthion is equally toxic to insects and its chemical properties and solubility and hydrolysis are similar to those of parathion. Chlorthion ® has a long residual life for a phosphate.

Ronnel

Ronnel is an excellent animal systemic insecticide. It is also known as fenchlorphos, Etrolene, Dow-ET-57, ET-14, Korlan, and Trolene. It is crystalline and melts at 40-41°C.



O,*O*-DIMETHYL *O*-2,4,5-TRICHLOROPHENYL PHOSPHOROTHIOATE

- Ronnel is relatively soluble in water and is soluble in most organic solvents. It has a mild mercaptan odor.
- It is a very safe insecticide.
- It is administered orally and is effective against many ecto- and endoparasitic arthropods including cattle grubs, screw worms, and sucking lice.
- It is also used as a residual spray for controlling flies, fleas, and cockroaches.
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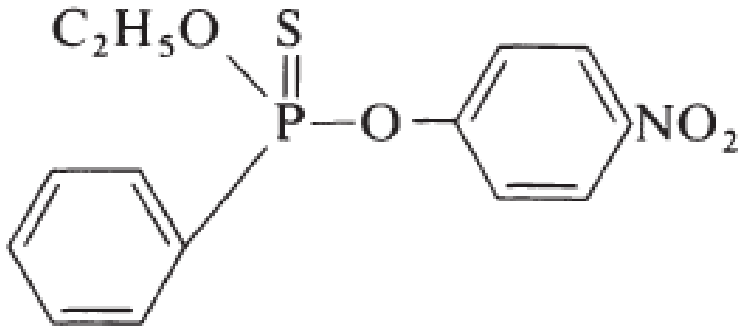
- Its phytotoxicity limits its use as a forage and crop spray agent.

EPN

It is the "tail" part of the compound that is important in determining toxicity and selectivity.

EPN, a phosphonate, is different, for it has a direct carbon-phosphorus link. EPN was introduced in 1949.

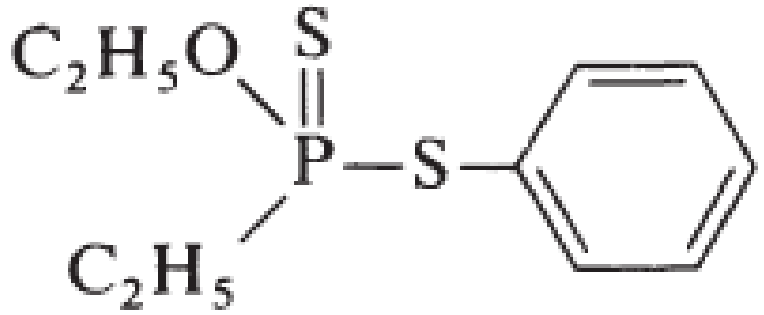


O-ETHYL *O*-*p*-NITROPHENYL PHENYLPHOSPHONOTHIOATE

- ❖EPN is a white crystalline solid with a melting point of 36°C.
- ❖Technical EPN is a dark amber liquid.
- ❖It is hydrolyzed in alkali to p-nitrophenol.
- ❖It is less volatile than parathion.
- ❖EPN is relatively toxic to mammals and is an acaricide in addition to being an insecticide.
- ❖It is an excellent insecticide and acaricide for orchard pests, including apple flea weevil, plum curculio, and coddling moth, and for some soil insects.

Fonofos

Fonofos is produced by Stauffer Chemical Co. It is an effective soil insecticide. It is used for control of corn rootworms, wireworms, cutworms and other soil pests.



ETHYL-*S*-PHENYLETHYLPHOSPHONOTHIOLOTHIONATE

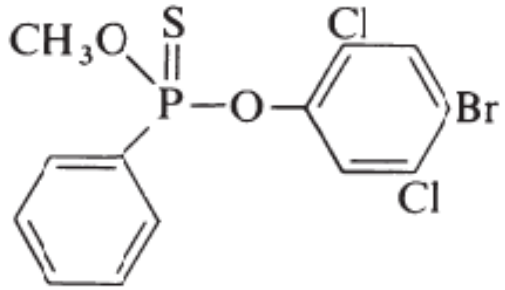
Leptophos

This compound is stable and persists in plants and it is particularly useful for lepidopteran insects.

It has some fungicidal effects. It is effective against pests on cotton, rice, and tobacco.

It is the probable cause for massive delayed neurotoxicity cases of poisoning of water buffaloes in Egypt.

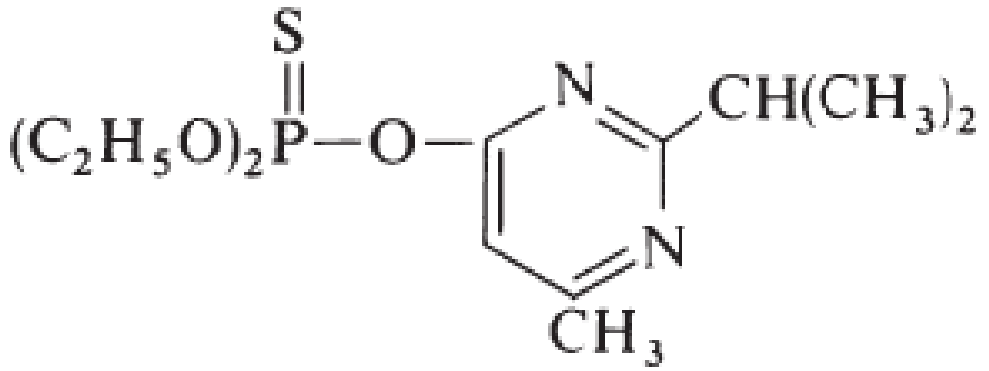
It is of interest as an agent producing delayed neurotoxic symptoms in experimental animals.



O-(4-BROMO-2,5-DICHLOROPHENYL) *O*-METHYL PHENYLPHOSPHONOTHIOATE

Diazinon

Diazinon is an important insecticide which is widely used today. It has a relatively low mammalian toxicity. Geese and ducks, however, are very susceptible to diazinon poison.



O,*O*-DIETHYL *O*-(2-ISOPROPYL-6-METHYL-4-PYRIMIDINYL) PHOSPHOROTHIOATE

Diazinon is a colorless liquid with a boiling point of 83-84°e.

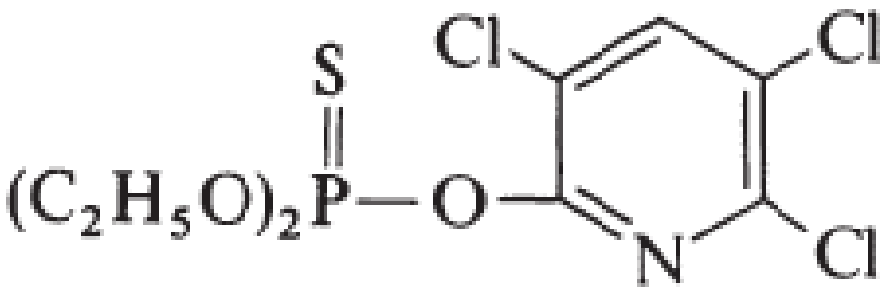
The technical product is a brown liquid. It is sensitive to oxidation and heat, quickly degrading at temperatures.

It is relatively stable in dilute alkali but is slowly hydrolyzed in water or dilute acid.

It has a wide spectrum of insect-killing power and can control various soil insects, DDT resistant flies, household pests, and various vegetable and forage crop insects.

Dursban

- Dursban is a residual organophosphate insecticide which has been effective in tests for controlling mosquitoes, ticks, soil and aerial insects on field crops, and household pests. Dursban ® is moderately toxic to animals



O,*O*-DIETHYL *O*-(3,5,6-TRICHLORO-2-PYRIDYL) PHOSPHOROTHIOATE