

Paper : - Pesticide Chemistry

Carbamates:

Mode of action – carbaryl, carbofuran, methomyl, aldicarb and bendiocarb characteristics and use persistence in plant, soil and water. Carbamates are derivatives (esters) of carbamic acid. Several carbamates are systemic, transported in the xylem. It is possible to control pests on shoots and roots which are otherwise difficult to reach. Hence, they are used as soil insecticides and nematicides (aldicarb, carbofuran, oxamyl etc.). Commercial products available are grouped into three groups.

1. N, N-dimethyl carbamates of enols and hydroxy heterocycles
2. Phosphocarbomates
3. Oxinecarbomate

Widely used as:

- they are **more degradable** than organophosphates
- they have **lower dermal** toxicities. Mostly absorbed via inhalation, ingestion

Mechanism of action

The mechanism of action of the insecticidal carbamates is identical to that of the organophosphates, viz., inhibition of the enzyme cholinesterase. This enzyme has the function of hydrolyzing the post synaptic effector, acetylcholine into choline and acetic acid. Inhibition of acetylcholinesterase (ACHE) leads to a buildup of acetylcholine in the post synaptic membrane and hence to a permanent nerve stimulation with lethal results. This stimulation of insects manifests itself in uncontrolled movements and paralysis.

OR

- **Mode of action:** toxicity due to **inhibition of acetylcholinesterases** - however unlike the organophosphates they do not need to be modified (**S** --> **O**) before becoming effective.

- They do not penetrate the CNS so most effects are respiratory in nature. Depression of respiration combined with pulmonary edema is the usual cause of death from poisoning by N-methyl carbamate compounds.
- **The N-methyl carbamate esters cause reversible carbamylation** of acetylcholinesterase enzyme, allowing accumulation of acetylcholine, the neuromediator substance, at parasympathetic neuroeffector junctions (muscarinic effects), at skeletal muscle myoneural junctions and autonomic ganglia (nicotinic effects), and in the brain (CNS effects).
- **The carbamyl-acetylcholinesterase combination dissociates more readily than the phosphoryl-acetylcholinesterase complex produced by organo-phosphate compounds.** This liability has several important consequences:
 - 1) it tends to limit the duration of N-methyl carbamate poisonings,
 - 2) it accounts for the greater span between symptom-producing and lethal doses than exists in the case of most organophosphate compounds, and
 - 3) it frequently invalidates the measurement of blood cholinesterase activity as a diagnostic index of poisoning as it disassociates rapidly enough not to be detectable...although toxicity had occurred earlier with exposure....

Synthesis of insecticide Sevin

Introduction

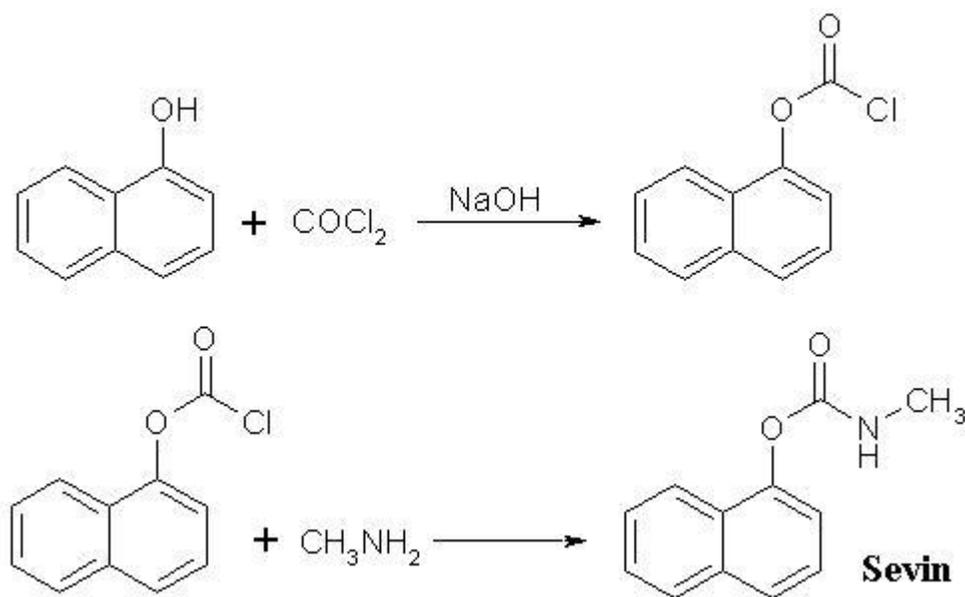
Carbaryl is a wide-spectrum carbamate insecticide which controls over 100 species of insects on citrus, fruit, cotton, forests, lawns, nuts, ornamentals, shade trees, and other crops, as well as on poultry, livestock and pets. It is also used as a molluscicide and an acaricide. Carbaryl works whether it is ingested into the stomach of the pest or absorbed through direct contact. The chemical name for carbaryl is 1-naphthol N-methylcarbamate. Carbaryl is formulated as a solid which varies from colorless to white to gray, depending on the purity of the compound. The crystals are odorless. This chemical is stable to heat, light and acids under storage conditions. It is non-corrosive to metals, packaging materials, or application equipment. It is found in all types

of formulations including baits, dusts, wettable powder, granules, oil, molassas, aqueous dispersions and suspensions.

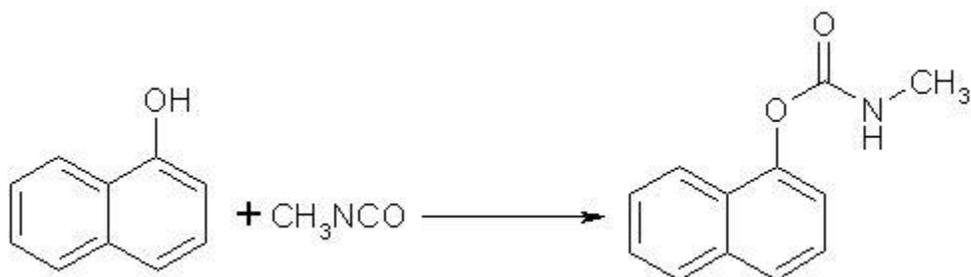
(Naphthyl carbamate, 1-Naphthyl-N-methyl carbamate) LD50: 850 mg. Broad spectrum contact insecticide, non-systemic used in cotton, fruits, vegetables, forage crops etc. Also to control of earth worms. Carbaryl, introduced by American Union Carbide Company in 1956 was the first successful commercial carbamate. Carbaryl is produced by any of the general methods of preparation of carbamates, like reacting 1-naphthol with methyl carbamoyl chloride at room temperature. The rate of reaction is increased by removing the HCl that is formed with a stream of air or nitrogen. Pure compound of carbaryl is obtained by reacting 1-naphthol with methyl isocyanate. Carbaryl is also synthesized by reacting 1-naphthylchlorocarbonate with methylamine in the presence of HCl acceptors. Carbaryl is a white crystalline compound with M.P. 142° C. it is highly soluble in organic solvents; resistant to the action of water at room temperature and also to light and oxygen of air. In alkaline medium, it is rapidly hydrolysed and so it is not compatible with compounds of alkaline nature like Brodeaux Mixture.

Routes of Sevin synthesis:

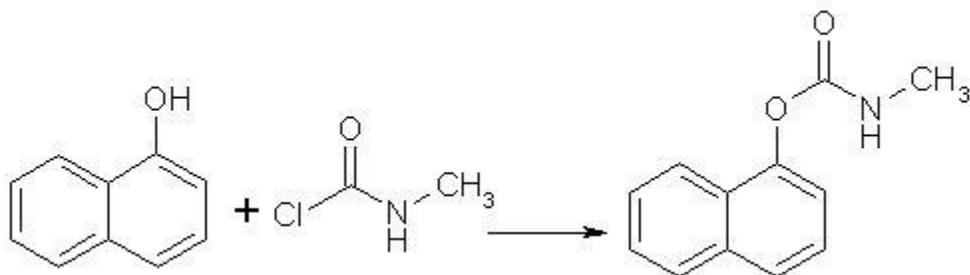
1) With using naphthol-1 and phosgene:



2) With using naphthol-1 and methyl isocyanate:



3) With using naphthol-1 and methylcarbamoyl chloride:



Reference

<http://www.exchemistry.com/sevin.html>

pesticide chemistry by Cremlyn

Carbofuran (Furadan)

(2, 3, dihydro 2, 2 dimethyl 7, benzofuranyl) Broad spectrum insecticide, nematicide and miticide. LD50: 8-14 mg/kg rat. Can be incorporated in soil at 6-10 kg/ha for control of soil insects and nematodes. It has high mammalian toxicity but is rapidly metabolized to non-toxic products in plants and animals. It is a systemic carbamate, broad spectrum insecticide. It is stable in acid and neutral media but unstable in alkaline medium. Sparingly soluble in water; but soluble in organic solvents. It is compatible with non-alkaline pesticides and fertilizers. It is not phytotoxic to rice. Carbofuran when applied to soil is absorbed by plant roots and distributed to stems and leaves and metabolized to non-toxic compounds in 30 days. Carbofuran present in soil is degraded by hydrolysis depending on soil pH and clay content. Toxic residues do not remain in the soil for long.

Carbofuran

- Corn rootworm insecticide
- Oral LD₅₀
 - ≤ 8 mg/kg in rats (po)
 - 11 mg/kg in humans
 - ~ 1 mg/kg in birds
- Environmental Effects:
 - Loses effectiveness due to increasingly rapid microbial degradation

