ABSTRACT

The development of organophosphorus pesticides has resulted from the researches of Professor Schrader in Germany just prior to the second world war, and has had a profound influence upon the chemical control of pests. Extensive research in the field has led to the discovery of several compounds with pesticidal properties of every description. Because of their low persistency and high effectiveness, organophosphorus pesticides are now used widely in the world. Thus several organophosphorus compounds are or were used as chemical pesticides, which include the organophosphorus compounds of fungicidal, insecticidal, acaricidal, nematocidal, anthelmintic, insect sterilizing, herbicidal, rodenticidal and plant growth regulating activities.

The work embodied in this dissertation is related to the investigation of some nitro-aliphatic cyclic amidophosphorothioates with reference to their fungicidal, insecticidal, chemical and other properties along with the structural elucidation by chemical analyses and spectroscopic methods.

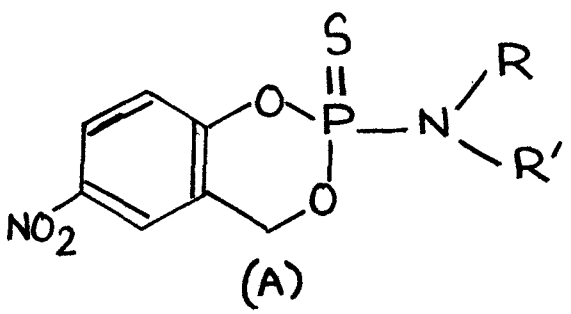
In Chapter-I of this dissertation, a general introduction including NMR, IR, Mass spectra, anticholinesterase activities and chemical hydrolysis of some

organophosphorus pesticides has been presented; common or trade names, chemical structures and other properties of some of them have been given in Appendix -I.

PART-II of this thesis has been devoted to a review of antibiotin cyclic phosphorous compounds with special emphasis on salithion (2-methoxy-4H-1,3,2-benzodioxaphosphorin-2-sulphide) having a unique cyclic structure, discovered by Prof. Eto, Prof. Ishima and their co-workers in 1963. Salithion, a broad spectrum insecticide, was commercially manufactured by Sumitomo Chemical Co. of Japan in 1966. Since then several other antibiotin cyclic phosphorous esters e.g., phosphates, phosphorothiolates, phosphoramidates, phosphonates and their thiono-analogs have been synthesised and examined for pesticidal activities. Investigation has revealed that the biological activities of these compounds are greatly influenced by the exocyclic substituents on the phosphorous atom and also by the substituents in benzene or in hetero-cyclic ring.

It has been reported by Prof. Eto and his co-workers that introduction of an amide group in place of an alkyl ester group often gives organophosphorous esters fungicidal, nematocidal and other biological

activities. There are many examples in literature which show that some phosphoramidothionates, phosphoramides or phosphonamides, in which the phosphorous atom is attached directly to the nitrogen atom of an amine or a heterocyclic compound such as phthalimide, indazole or triazole, have very good fungicidal properties. These observations prompted us to undertake a systematic work on some substituted saligenin cyclic phosphorous compounds. The work embodied in PART-III of this dissertation is related to the investigation of some 6-nitro-saligenin cyclic amido-phosphorothionates having general structure (A)



(A)

where - NRR' = cyclohexylamido, morpholino, diethylamido, dimethylamido and isopropylamido groups.

The structures of these compounds have been established by chemical analysis, UV, mass, IR and NMR spectral data. All the compounds show common IR

bands for P-O-alkyl, P-O-aryl and for nitro group. They show common parent molecular ion in mass spectra. From the study of the PMR spectral data of some 2-alkoxy/phenoxy/anilo-6-nitro-4H,1,3,2-benzodioxaphosphorin-2-sulphides it is fairly evident that the chemical shift difference of the protons H_{4A} and H_{4B} (of the $-CH_2-$ group in the dioxaphosphorin ring) increases in going from 2-alkoxy to 2-alkylanilo compounds, and that the 2-substituent at the same time increases in bulk and probably spends more time in the conformation with the least steric interaction. Several plot expansion and decoupling experiments show that one conformation seems less hindered for bulky 2-substituent groups than the other conformer.

All the anilo thiophosphorothionates are fungitoxic to the fungi H. oryzae and A. sp. For H. oryzae the diethylanilo compound is most active and for A. sp. the morpholino compound. None of the compounds are phytotoxic to Triticum sp. upto 500 ppm. Among the five compounds the dimethyl anilo compound has the highest oral insecticidal activity to cockroaches, but its insecticidal activity is less than that of malathion. All compounds are less toxic to rats than malathion. The anti-acetylcholinesterase activity (for which) of the

dimethylamido compound is highest, and that of the diethylamido compound is least. On the other hand, the anticholinesterase activity (for blood-ch) of the morpholino compound is most, and that of the dimethylamido compound is least. From the chemical hydrolysis study it has been observed that the amidophosphorothionates having the tertiary amido groups are extremely resistant to hydrolysis compared to other compounds having the secondary amido groups.

The biological properties and other data justify further examination of these nitro-analogs in cyclic amidophosphorothionates and other related compounds as potential pesticides.