PART I

PART - I

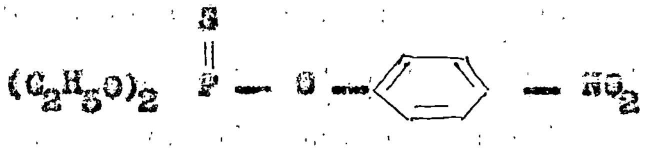
ORGANOPHOSPHORUS PESTICIDES : GENERAL INTRODUCTION

1. INTRODUCTION :

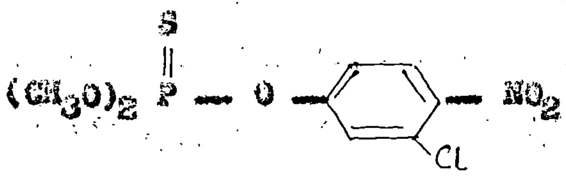
The pest, disease and weed situation are not static - they keep on changing. New physiological races evolve as a result of mutations in nature. Many insects and fungi develop resistant strains when the same insecticide or fungicide is used year after year. Similarly, by the use of the same herbicide, season after season there is often a shift in the weed flora and a number of resistant species become predominant. Even change in croping pattern change the pest, disease and weed situation - many pests, diseases and weeds of minor importance may assume major proportions. It has been often noticed that pests and diseases, virtually unknown and ignored suddenly become very alarming with the introduction of new crop varieties. Bacterial blight, tungrovirus, gall midge of paddy and Phalaris minor in wheat are only a few examples from our country.

All these definitely point out that the existing pesticides, however efficient they may be cannot solve the pest problems permanently. New pesticides must be developed to combat various new situations. It should be a continuous search - a process of intensive and sustained research and development. Apart from finding answers to new problems, research and development are also vital for finding pesticides which will be safer, more effective and selective, and above all more economic in the true sense and environmentally acceptable.

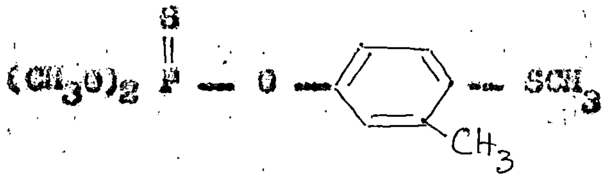
A particularly important group of pesticidal substances comprises phosphorus compounds, the importance of which have been steadily increasing in the recent past. Several new compounds of this group are used for insecticidal, acaricidal, nematocidal, anthelmintic, insect sterilizing, fungicidal, herbicidal, rodenticidal and other purposes. The development of new phosphorus compounds was for a long time dominated almost exclusively by one single guiding principle namely the 'Acyl Rule' of Schrader (1,2,3). The great advancement in agricultural practice, scientific knowledge of the structure-activity relationship and mode of action of organophosphorus pesticides were achieved by the discovery of parathion by Schrader in 1944. Parathion is extremely toxic to mammals as well as to insects. Many less toxic pesticides have been synthesized by slight structural modification of parathion; for example, chlorthion (in 1952), fenthion (in 1958) and fenitrothion (in 1959) were discovered (3).



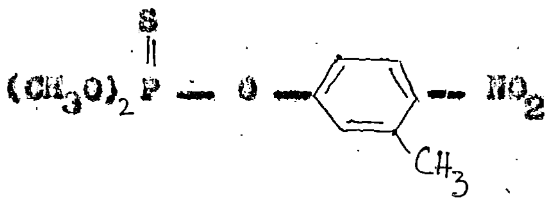
Parathion



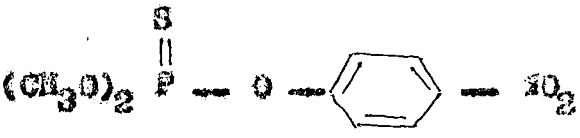
Chlorthion



Fenthion

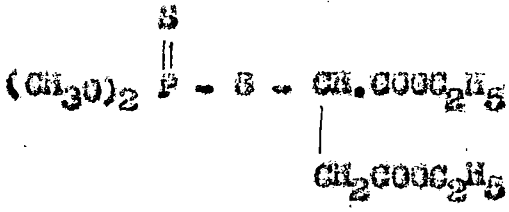


Fenitrothion



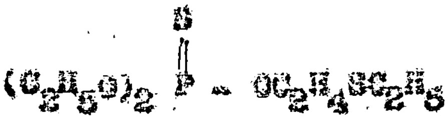
Parathion - methyl

Malathion was discovered in 1950 and demeton in 1951.



$$(CH_3O)_2\overset{S}{\overset{\|}{P}}-S-\underset{CH_2COOC_2H_5}{\underset{|}{CH.COOC_2H_5}}$$

malathion



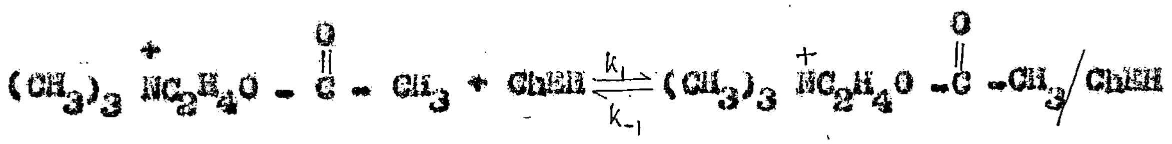
$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-OC_2H_4SC_2H_5$$

demeton - S

In 1952, the Perkow reaction was discovered, and many important vinyl phosphate esters have been introduced as practical pesticides. Since then several new compounds have been developed and are in commercial use (3). Common or trade names, chemical structures and other properties of several organophosphorus pesticides have been given in Appendix-I.

2. REACTION WITH CHOLINESTERASE:

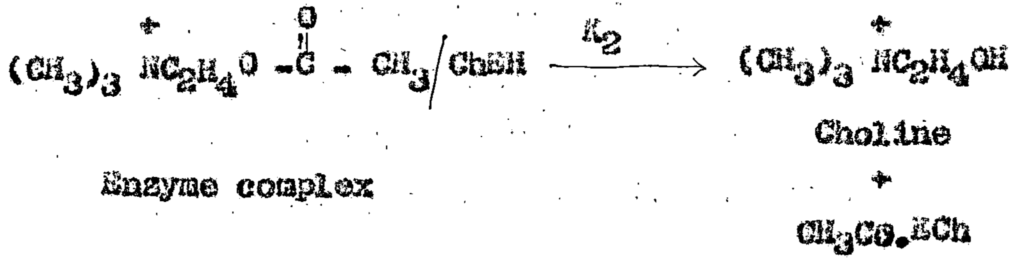
It is generally accepted that the organophosphorus compounds are toxic because they phosphorylate vital esterases, thus forming complexes that are either irreversible or do not readily release the enzymes (3). The enzyme mainly affected is accepted to be cholinesterase, an enzyme that plays a vital role in hydrolysing acetylcholine. The reaction between acetylcholine (Ach) and cholinesterase (ChEH) takes place in three stages:



$$(CH_3)_3\overset{+}{N}C_2H_4O-\overset{\overset{O}{\|}}{C}-CH_3 + ChEH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3\overset{+}{N}C_2H_4O-\overset{\overset{O}{\|}}{C}-CH_3/ChEH$$

Acetylcholine Enzyme complex

At this stage there is an equilibrium between the enzyme and its substrate on the one hand and a complex of the two on the other.



$$(CH_3)_3\overset{+}{N}C_2H_4O-\overset{\overset{O}{\|}}{C}-CH_3/ChEH \xrightarrow{K_2} (CH_3)_3\overset{+}{N}C_2H_4OH + CH_3CO.ECh$$

Enzyme complex

Choline

Acetylated enzyme

The complex yields choline and acetylated enzyme in the second stage.

$$CH_3CO.ECh \xrightarrow[K_3]{H_2O} CH_3COOH + ChEH$$

Acetylated enzyme Acetic acid enzyme

The final stage is the deacetylation reaction in which the acetylated enzyme is hydrolysed to give the free enzyme and acetic acid.

The active center of acetylcholinesterase (AChE) is structurally complementary to its substrate acetylcholine which contains a trimethyl ammonium group with a positive charge on N and an ester linkage. The enzyme's active center contains a negatively charged anionic site, which binds the trimethylammonium group, and a relatively "nonspecific" esteratic site, which catalyzes the hydrolysis of the ester linkage. In the ~~xxx~~ esteratic site there are basic (histidine, imidazole), serine hydroxyl, and acidic (tyrosine hydroxyl) groups (Fig. 1). The reaction between paraoxon and AChE is represented in Fig. 2. When the two chemicals interact there is a nucleophilic attack of the serine hydroxyl on the phosphorus atom that is aided by the acidic and basic groups present in the esteratic site of the enzyme. This results in the formation of a "reversible" complex that finally yields phosphorylated enzyme and p-nitro~~[illegible]~~ saligenin. Aldridge(4) investigated the inhibition of cholinesterase by parathion and related compounds and found that the complex did not show significant reversibility. In other words, the inhibition of cholinesterase in this case followed first order kinetics and was bimolecular, i.e. :

$$K = \frac{1}{tI} \ln \frac{100}{b}$$

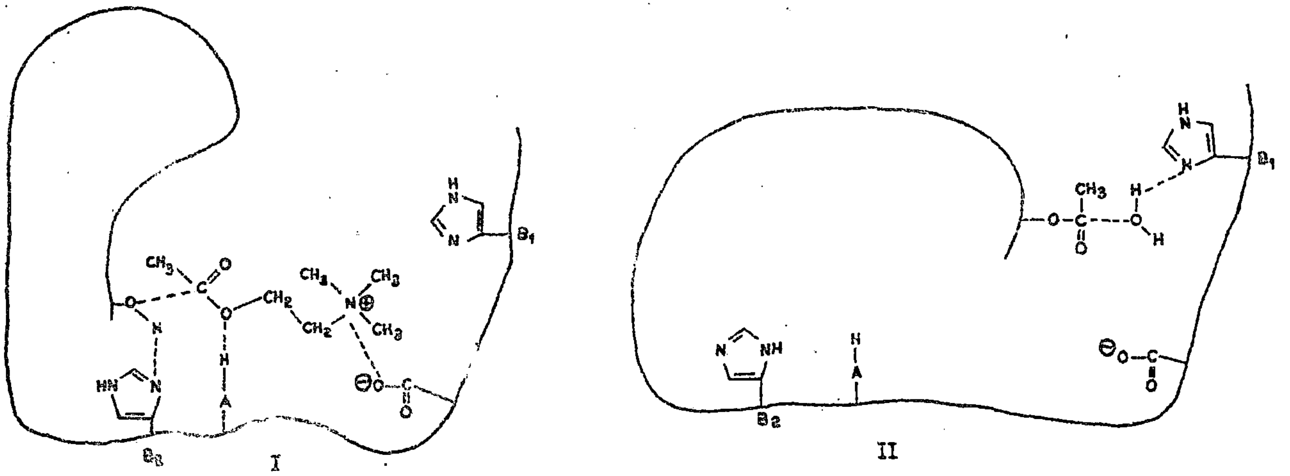


Fig. 1. Schematic Mechanism of action of AChE, after Krupka.
(I) Enzyme-substrate complex in AChE.
(II) Deacetylation of acetyl-AChE.

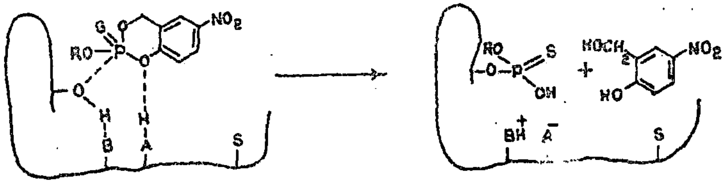


Fig. 2. Schematic mechanism of reaction of organophosphate with AChE.

where K = bimolecular rate constant,

t = time in minutes,

I = molar inhibitor concentration,

and, b = percentage residual activity.

Correlation between the reactivity of a organophosphorus compound and its cholinesterase inhibition, however, has not been ideal, and Main(5) introduced a kinetic treatment for the reaction that takes into account the reversibility of the complex. This reversibility is dependent on the affinity of the inhibiting compound for the active site of cholinesterase as well as on the rate of phosphorylation (Fig. 2). By utilizing different kinetic methods the values for K_1 (affinity constant), k_p (phosphorylation constant), and k_e (bimolecular inhibition constant) may be determined(5,6).

If the acetylcholinesterase is destroyed, is irreversibly bound, or forms a complex from which it is released more slowly than under normal conditions, its substrate, acetylcholine, is not easily removed from the receptor surface of the muscle. This causes the muscle to be depolarised longer than usual and gives rise to several action potentials passing through the muscle. The result is a twitching of the muscle leading to tetanus and eventual paralysis of the muscle. Death in mammals occurs as a result of asphyxia caused by the paralysis of respiratory muscles.

3. CHEMICAL HYDROLYSIS:

Since most organophosphorus pesticides hydrolyse, their persistence and/or appearance of hydrolysis products may be obtained from kinetic studies. Hydrolysis rates of these compounds and their metabolites are of interest since chemical hydrolysis determines whether or not toxic residues will persist. The first-order half-lives of some common organophosphorus pesticides including some metabolites are listed in Table - 1 (7).

Table - 1.

Half-lives of some Organophosphorus Pesticides in Ethanol (Tem.70°C, pH 6.0, Buffer Solution (1:4)

Compound	Half-life hours	Compound	Half-life hours
Thimet oxon	0.60	Demeton-s	18.0
Dichlorvos	1.35	Morphothion	18.4
Thimet	1.75	Baytex	22.4
Trichlorphon	3.2	Vamidothion	25.4
Mecarbam	5.9	Menazon	27.6
Malaoxon	7.0	Paraoxon	28.0
Demeton-S-methyl	7.6	Thionazin	29.2
Malathion	7.8	Disulfoton	32.0
Thionazin-oxon	8.2	Diazinon	37.0
Parathion methyl	8.4	Ethion	37.5
Fenchlorphos	10.4	Parathion	43.0
Azinphosmethyl	10.4	Phenkapton	92.0
Sumithion	11.2	Chlorfenvinphos	93.0
Dimethoate	12.0	Carbophenothion	110.0
Thiometon	17.0	Dimefox	212.0
Methyl oxy-demeton	17.1		

The hydrolysis rate is dependent upon the chemical structure and reaction conditions such as pH, temperature, the kind of solvent used, and the existence of catalytic reagents(3). In aqueous solution, between the pH range 1 to 5 many organophosphorus pesticides are most stable(8), and in this range (pH 1 to 5), the variation in pH of the solution has practically no effect on the hydrolysis rate. But the hydrolysis rate increases steeply at pH higher than 7, and all organophosphorus pesticides are much more unstable under alkaline conditions. Very good discussions on chemical structure and hydrolyzabity of various organophosphorus pesticides are given by Eto(3) and Faust(7).

4. INFRARED SPECTRA:

The IR spectra-structure correlations of organophosphorus compounds have been given by several workers(9-14). The first set of organophosphorus group frequency correlations were furnished by Meyrick and Thomson(9) and by Gore(10). These were based on relatively few compounds. By 1964 Thomas and Chittendan(11) were able to start publishing correlations based on data from 2300 compounds and by 1970 these workers(12) were able to publish organophosphorus group frequency correlations based on data from over 4000 compounds. Thomas(13) has recently revised all the existing correlations in the light of data from 5600 organophosphorus compounds. As a result of this, Thomas(13) has been able to demonstrate that by systematic applications of the correlations, it is possible to deduce a great deal of the structure of an unknown organophosphorus compound on the basis of the IR spectrum. By the application of the correlations given by Thomas (13), Das (14) has been able to deduce the structures of 110 organophosphorus pesticides. A full list of correlations which have been proposed is given in the Table - II.

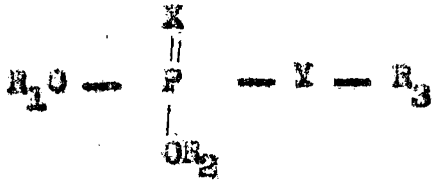
Table - II

a) Phosphorus-Oxygen Links:	
i) $P = O$ (free)	1350-1250 cm^{-1} (s)
$P = O$ (hydrogen bonded)	1250-1110 cm^{-1} (v.s)
ii) P-O-C (aliphatic)	1050-990 cm^{-1} (v.s.) and near 1150 cm^{-1}
P-O-C (ethyl)	1092-1008 cm^{-1} (v.s.) and 1170-1150 cm^{-1} (w)
P-O-C (methyl)	1060-1015 cm^{-1} (v.s.) and 1190 ± 10 cm^{-1} (w)
iii) P-O-C (aromatic)	1240-1190 cm^{-1} (s) and 995-850 cm^{-1} (s)
iv) P-O-P	970-900 cm^{-1}
b) Phosphorus-Sulphur Links:	
$P = S$ (I)	862-674 cm^{-1}
$P = S$ (II)	730-550 cm^{-1}
c) Phosphorus-Carbon Links:	
i) P - phenyl	1460-1425 cm^{-1} (m)
ii) P - alkyl	No useful correlations.
$P - CH_3$	1320-1280 cm^{-1}
d) Phosphorus-Halogen Links:	
$P - Cl$	580-440 cm^{-1} (s)
e) Phosphorus-Nitrogen Links:	
$P - N$	1665-870 cm^{-1}

It should be stated at once that not all of these correlations are of equal value, and that, whilst many of them are based upon the examinations of large number of compounds, others are only very tentative correlations based on a few compounds or on compounds of a limited type. The basis of each of these correlations has been well discussed by Thomas (13).

5. NMR SPECTRA:

The NMR spectra-structure correlations of organophosphorus compound have been given by several workers (15-18). Babad et al (15) and Keith et al (16) reported the NMR spectra of some organophosphate insecticides in $CDCl_3$. Coupling constants and chemical shifts of some methyl and ethyl substituted organophosphate insecticides are given in Table-III and Table-IV. For compounds,



$$R_1O - \overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle OR_2}{|}}{P}} - Y - R_3$$

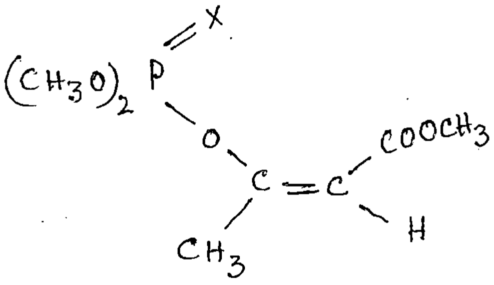
(1)

where R_1 and R_2 are both methyl groups, the methyl peak appears in the region $\delta = 3.9$ to 3.7 ppm with $J(P-CH_3) = 11$ to 16 Hz. Organophosphates in which R_1 and R_2 are both ethyl show methyl peaks at $\delta = 1.4$ and methylene peaks in the region $\delta = 4.2$ to 4.4. In this case, the $J(P-CH_3)$ and $J(P-CH_2)$ coupling constants are 0.8

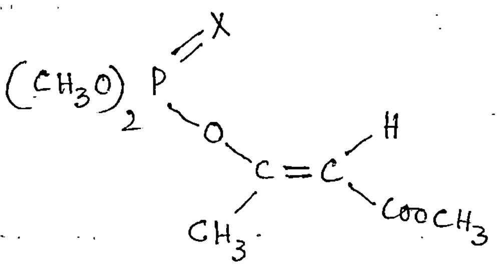
and 10 Hz. The chemical shifts of methyl and ethyl protons are quite comparable, between oxygen-containing organophosphate compounds and their sulfur analogs, but the coupling constants are something higher for compounds with a P = S bond than that with a P = O bond.

In many cases, it has been observed a further splitting in both the methyl proton peaks as well as methylene peaks. (Table-III & IV). This has been explained by Keith et al (16) on the basis of magnetic non-equivalence of methyl protons due to hindered rotation around one or more bonds of the phosphorus atom.

The cis-trans isomerism of organophosphorus compounds has also been detected by NMR. Isomerism is found when phosphorus is attached, by oxygen or sulfur, to a carbon-carbon double bond. The cis and trans isomers of phosdrin and its sulfur analogs are represented by the formula (2) and (3) and their coupling constants and chemical shifts are shown in Table-V.



(2)



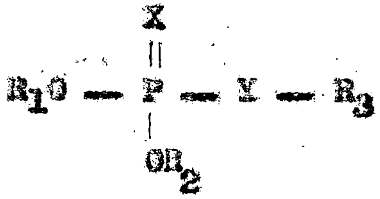
(3)

X = O or S

Some interesting results have been reported for phosphoramidate type compounds in which X is a nitrogen atom. The NMR spectrum in the methyl region, when two methyl groups are attached to the nitrogen exhibits a pattern characteristic of hindered rotation around the partial carbon-

Table - III

Chemical shifts and coupling constants for methyl groups in various organophosphates.



$$R_1O - \overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle OR_2}{|}}{P}} - Y - R_3$$

(1)

Compound	R_1	R_2	R_3	X	Y	δCH_3	$J(P-CH_3)$ Hz
Bidrin	Me	Me	N,N-dimethyl cis-crotonamide	O	O	3.83	11.0
Ciodrin	Me	Me	∝-methyl benzyl cis-crotonate	O	O	3.8	11.0
DDVP	Me	Me	2,2-dichlorovinyl	O	O	3.86	11.0
Dicapthon	Me	Me	2-chloro-4 nitro phenyl	S	O	3.92	14.0
Dimethoate	Me	Me	N-methylcarbamoylmethyl	S	S	3.8	15.0
Dimethoxon	Me	Me	N-methylcarbamoylmethyl	O	S	3.83	12.5
Guthion	Me		4-oxo-1,2,3 benzotriazin-3(4H)-yl-methyl	S	S	3.76	15.0

Contd..........

Table - III (Contd.....)

Compound	R_1	R_2	R_3	X	Y	δCH_3	$J(P-CH_3)$ Hz
Guthion (Oxygen analog)	Me	Me	4-oxo-1,2,3 benzotriazin-3(4H)-yl-methyl	O	S	3.81	12.0
Imidan	Me	Me	Phthalimidomethyl	S	S	3.77	15.0
Malaxon	Me	Me	1,2 dicarbethoxyethyl	O	S	3.83 3.82	13.0
Malathion	Me	Me	1,2 dicarbethoxyethyl	S	S	3.81 3.8	15.5
Meta-Systox R	Me	Me	2-(ethyl sulfinyl) ethyl	O	S	3.82	13.0
Methyl Parathion	Me	Me	4-nitro phenyl	S	O	3.87	14.0
Methyl Trithion	Me	Me	P-chlorophenyl thiomethyl	S	S	3.72	15.0
Naled	Me	Me	1,2 dibromo-2,2-dichloroethyl	O	O	3.92 3.91	12.0
Phosdrin	Me	Me	2-carbomethoxy 1-methylvinyl	O	O	3.75	11.0
Phosphamidon	Me	Me	2-chloro-2(N,N-diethylcarbamoyl)-1-methylvinyl	O	O	3.88 3.8	12.0
Ronnel	Me	Me	2,4,5 trichlorophenyl	S	O	3.9	14.0

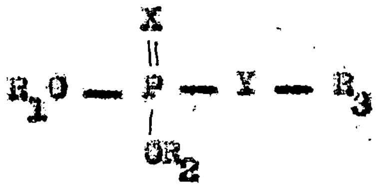
Contd.........

Table - III (Contd.....)

Compound	R_1	R_2	R_3	X	Y	δCH_3	$J(P-CH_3)$ Hz
Ruelene	Me	4-t-butyl-2-chlorophenyl	methyl	O	NH	3.81	11.0
Tiguvon	Me	Me	4-methylthio-m-tolyl	S	O	3.81	14.0
Trichlorofon	Me	Me	1-hydroxy-2,2,2-trichloroethyl	O	-	3.91 3.9	11.0
Zytron	Me	2,4-dichlorophenyl	isopropyl	S	NH	3.8	14.0

Table - IV

Chemical shifts and coupling constants for ethyl groups in various organophosphate (1)



$$R_1O - \underset{\underset{OR_2}{|}}{\overset{\overset{X}{\|}}{P}} - Y - R_3$$

(1)

Compound	R_1	R_2	R_3	X	Y	$\delta\,CH_3$	$J(P-CH_3)$ Hz	$\delta\,CH_2$	$J(P-CH_2)$ Hz
Co-Ral	Et	Et	3-chloro-4 methyl-2-oxo-2H benzopyran-7-yl	S	0	1.4	0.8	4.2	10.0
Diazinon	Et	Et	2-isopropyl-4-methyl 6-pyridinyl	S	0	1.38	0.8	4.34	9.5
Diazoxon	Et	Et	2-isopropyl-4-methyl 6-pyridinyl	0	0	1.39	1.2	4.33	8.0
Dioxathion	Et(2)	Et(2)	2,3-p-dioxane	S(2)	S(2)	1.36	-	4.17	10.0

Contd........

Table - IV (Contd......)

Compound	R_1	R_2	R_3	X	Y	δCH_3	$J(P-CH_3)$ Hz	δCH_2	$J(P-CH_2)$ Hz
Disulfoton	Et	Et	2-ethyl thioethyl	S	S	1.35	0.7	4.17 4.15	10.0
EPN	P-nitro phenyl	Et	Phenyl	S	-	1.36	0.5	4.27	10.0
Ethion	Et(2)	Et(2)	methylene	S(2)	S(2)	1.36	0.8	4.2 4.18	10.0
Paraoxon	Et	Et	4-nitrophenyl	O	O	1.39	0.9	4.26	8.5
Parathion	Et	Et	4-nitrophenyl	S	O	1.37	0.8	4.25	10.0
Phencapton	Et	Et	methyl(2,5-dichlorophenylthio)	S	S	1.36	0.8	4.18 4.16	10.0
Phorate	Et	Et	methyl thioethyl	S	S	1.36	0.8	4.18 4.17	10.0
Thionazin	Et	Et	2-pyrazinyl	S	O	1.41	0.8	4.35	9.0
Trithion	Et	Et	4-chlorophenylthiomethyl	S	S	1.33	0.8	4.12 4.09	10.0

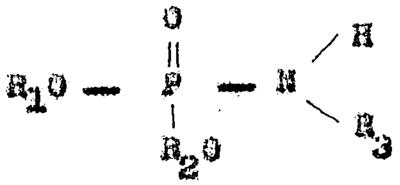
Table - V

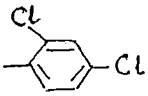
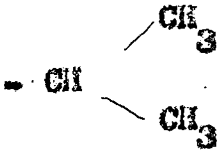
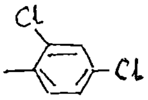
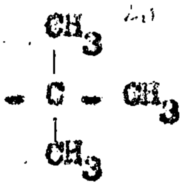
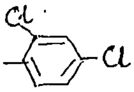
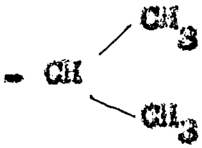
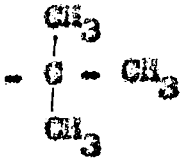
Chemical shifts and coupling constants in phosdrin isomers (2 and 3)

Compound	X	Chemical shift, δ				Coupling constant $J(CH_3-OP)$ Hz
		H	CH_3-O-P	CH_3O_2C	CH_3	
Cis Phosdrin	O	6.78	3.86	3.70	2.42	10.4
trans Phosdrin	O	5.30	3.88	3.67	2.15	11.2
Cis Thiono phosdrin	S	5.68	3.88	3.70	2.37	14.6
trans Thionophosdrin	S	5.36	3.82	3.67	2.10	14.6

Table — VI

Long-range coupling constants in phosphoramidates in $CDCl_3$ at Ambient temperature.



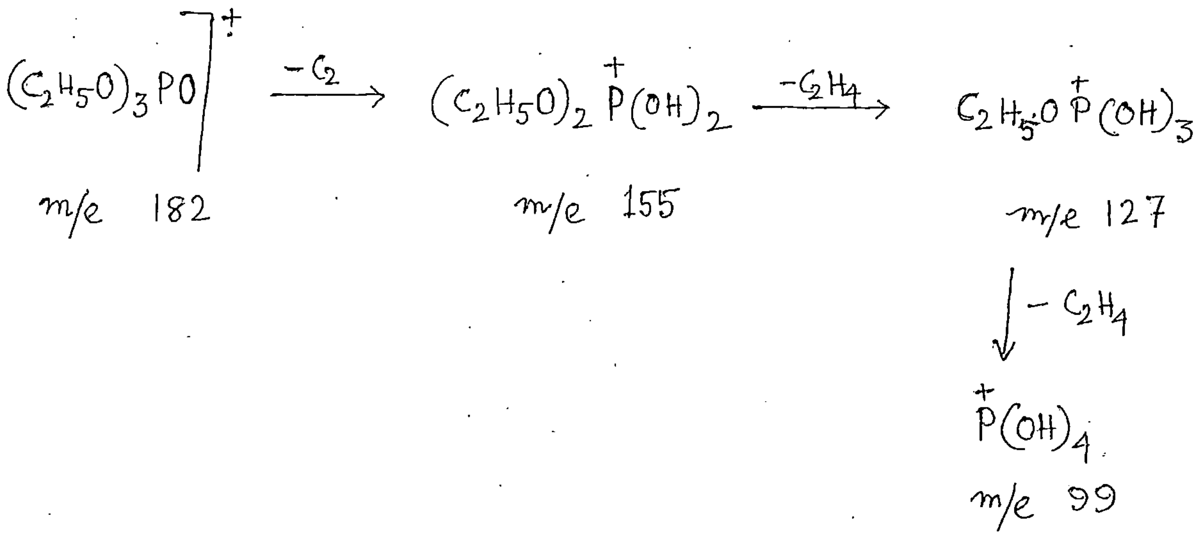
Substituent R_1	R_2	R_3	Coupling constant J(P-N-C-C-H) Hz
$-CH_3$			0.7
$-CH_3$		 $-C(CH_3)_3$	0.8
$-CH_3$		$-CH_2-CH_3$	1.0
$-C_2H_5$	$-C_2H_5$		0.7
$-C_2H_5$	$-C_2H_5$	 $-C(CH_3)_3$	0.7
$-C_2H_5$	$-C_2H_5$	$-CH_2-CH_3$	1.0

nitrogen double bond. The long-range $^{31}P - ^{1}H$ coupling constant $J(^{31}P - N - CH_3)$, although less than 1 Hz, is always observable (Table - VI).

6. MASS SPECTRA:

The mass spectra of several organophosphorus pesticides have been reported by Damico (19), Jörg et al (20), Gillis et al (21) and Eto (3).

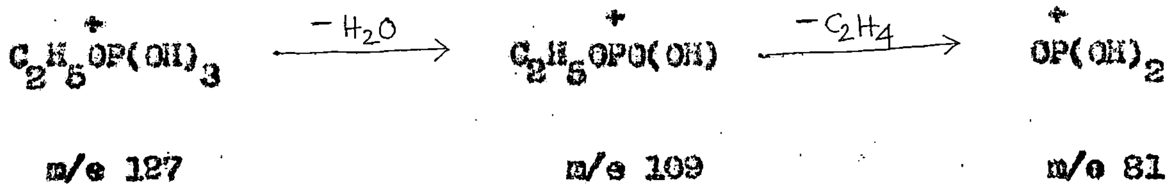
A significant rearrangement of two hydrogen atoms to phosphorus connected oxygens with the elimination of an alkyl group occurs at the first step of the fragmentation of trialkyl phosphates (3). For example, triethyl phosphate decomposes with the following consequtive elimination of two ethylene molecules, giving finally the intense peak of $P(OH)_4^+$ (m/e 99).



$$\left.(C_2H_5O)_3PO\right]^{\dot{+}} \xrightarrow{-C_2} (C_2H_5O)_2\overset{+}{P}(OH)_2 \xrightarrow{-C_2H_4} C_2H_5O\overset{+}{P}(OH)_3 \xrightarrow{-C_2H_4} \overset{+}{P}(OH)_4$$

m/e 182 → m/e 155 → m/e 127 → m/e 99

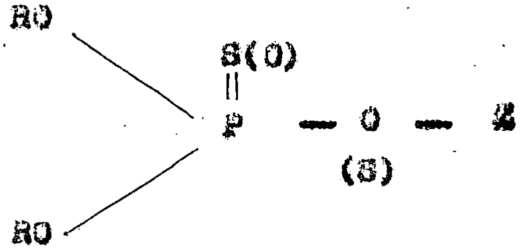
The fragment ion m/e 127 also decomposes in another way, accompanied by the elimination of water, as shown below:



$$\overset{+}{C_2H_5OP(OH)_3} \xrightarrow{-H_2O} \overset{+}{C_2H_5OPO(OH)} \xrightarrow{-C_2H_4} \overset{+}{OP(OH)_2}$$

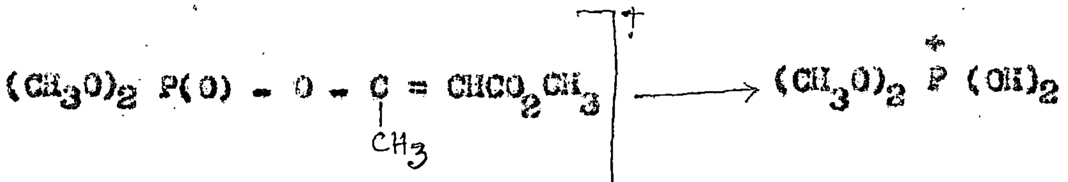
m/e 127 m/e 109 m/e 81

As the Z moiety of common organophosphorus pesticides shown below



is complex, the successive rearrangement-fragmentation does not always give the final ion $\overset{+}{P}(OH)_4$(m/e 99) or $(HO)_3PS\overset{+}{H}$ (m/e 115).

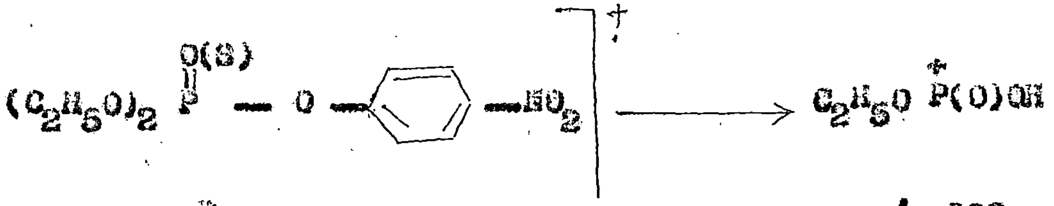
The base peak ion (m/e 127) for mevinphos and phosphamidon is postulated to be formed by the double hydrogen rearrangement mentioned above.



$$(CH_3O)_2P(O)-O-\underset{CH_3}{C}=CHCO_2CH_3\Big]^{+} \longrightarrow (CH_3O)_2\overset{+}{P}(OH)_2$$

mevinphos m/e 127

The mass spectrum of paraoxon is similar to parathion, and their base peak ion (m/e 109) is probably formed by the reaction shown below:

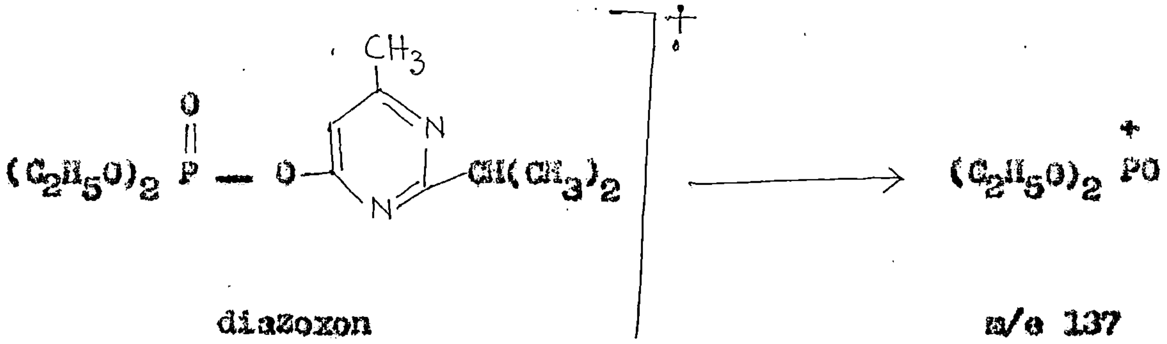


Paraoxon m/e 109

Paraoxon also gives relatively intense peaks of rearrangement fragment ions $\overset{+}{P}(OH)_4$ (m/e 99) and $OP(OH)_2^+$ (m/e 81). Another fragment ion, m/e 139 ($HO.C_6H_4\overset{+}{N}O_2$), may be formed due to α-cleavage of the molecular ion with hydrogen rearrangement.

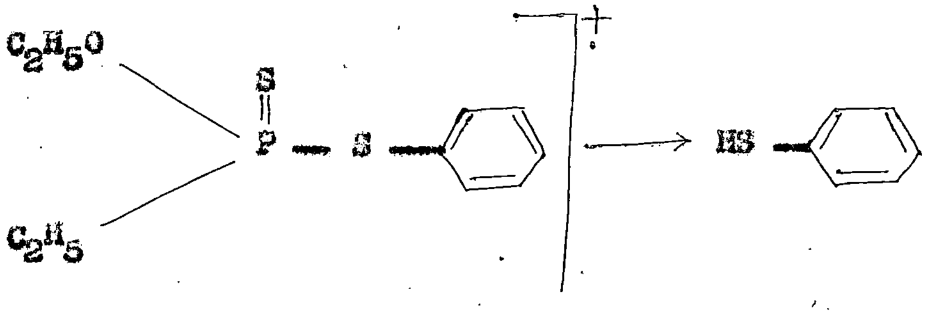
Dimethyl phosphorothionates such as parathion-methyl and fenitrothion also give a fragment ion of m/e 109. Moreover, these methyl esters, almost without exception, give fragment ions of m/e 125, 93, 79, 63 and 47.

Diazoxon forms a base peak ion (m/e 137) which is found probably due to α-cleavage. This type of fragmentation is most common with almost all phosphorus esters, including O,O-dialkyl phosphates, phosphorothionates, phosphorothiolates, phosphorodithioates, and also O-alkyl alkylphosphonodithioates such as fonofos.



diazoxon

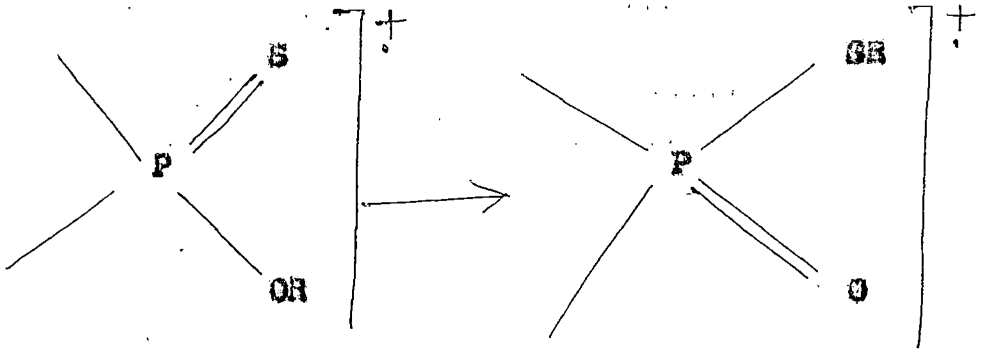
m/e 137



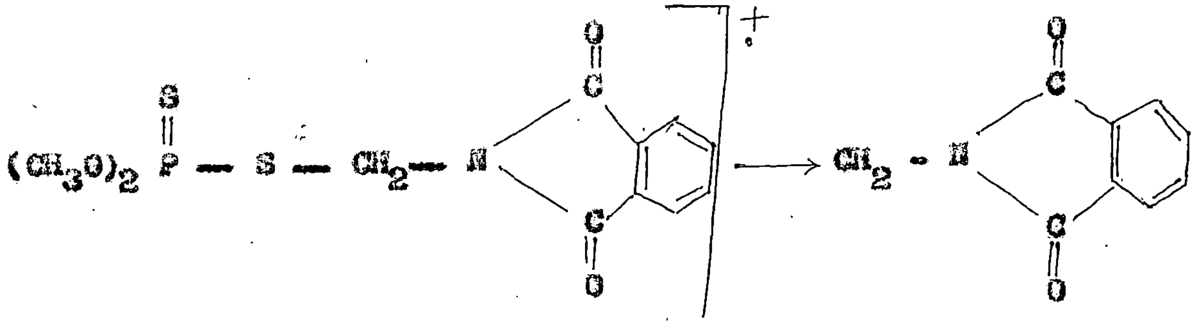
Fonofos

m/e 110

Cooks and Gerrard(22) observed that in case of some phosphorothionates a thiono-thiolo rearrangement may be induced by electron impact before any fission occurs:

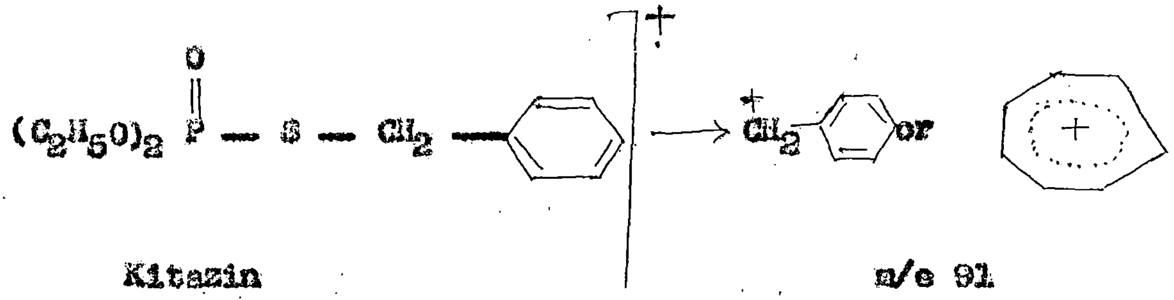


In organophosphorus pesticides having a P-S-alkyl(Z) bond, β-cleavage at the S-alkyl bond takes place very often to form a relatively intense peak with the charge on the Z moiety. The base peaks of malathion (m/e 173), phosmet (m/e 160), azinphosmethyl (m/e 160) carbophenothion (m/e 157), and kitazin (m/e 91) are all due to the β-cleavage.



Phosmet

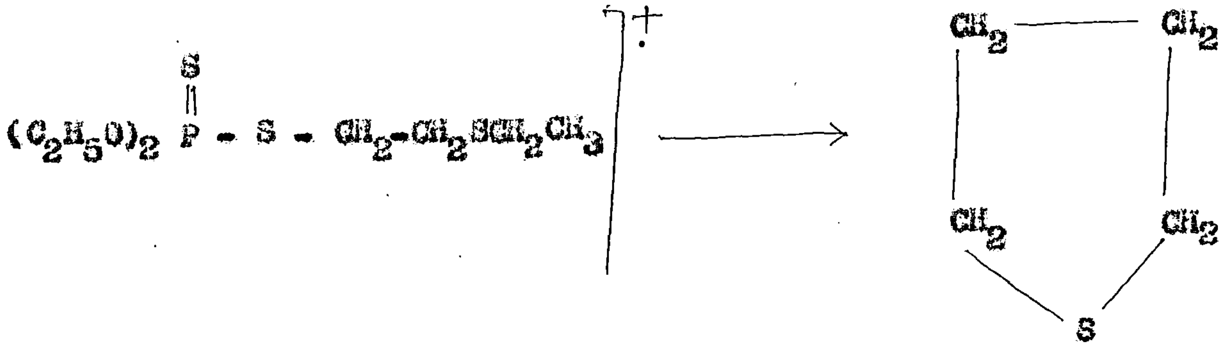
m/e 160



Kitazin

m/e 91

In some compounds, the β-cleavage occurs accompanied with rearrangement. The base peak of disulfoton (m/e 88) may be due to such a rearrangement forming tetrahydrothiofuran ion.



disulfoton

m/e 88

The CI (chemical ionization) mass spectra of several organophospherus pesticides were also reported (23). The determination of metastable transitions in the mass spectra of Abate and Dicapthon by direct analysis of daughter ions was also reported (24).

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