United States Patent Office 3,733,379 Patented May 15, 1973

3,733,379

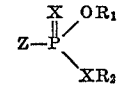
ALKOXYALKYL PHOSPHONATES

Karoly Szabo, Syracuse, N.Y., assignor to Esso Research and Engineering Company

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Int. Cl. A01n 9/36; C07f 9/40
U.S. Cl. 260—950 5 Claims

ABSTRACT OF THE DISCLOSURE

Organophosphorus compounds, characterized by the following structural formula:

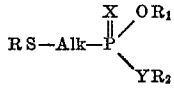


wherein Z is a C_1 to C_6 alkyl—O—CH_2 group; X is either O or S; R_1 is a C_1 to C_6 alkyl group; R_2 is one selected from the group consisting of C_1 to C_{20} aliphatic, C_6 to C_{10} aromatic and heretocyclic moiety containing 3 to 8 carbon atoms, have been shown to possess insecticidal properties.

This invention relates to novel organophosphorus compounds.

Under the prior art, many organophosphorus compounds are known to possess insecticidal activity.

For example, British Pat. 917,085 describes and claims a class of phosphorus compounds characterized by the following generic formula:

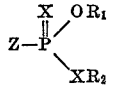


wherein Alk=C_1–C_4 alkylene; R and R_1 can be the same or different and each C_1–C_4 alkyl and R_2 is one selected from the group consisting of alkyl, phenylmercapto alkyl, alkylaminoalkyl, alkyl aminocarbonyl, optionally substituted phenyl, alkylmercapto or a coumaryl radical.

The disclosure in this patent is rather broad and relates to several $RSCH_2$-analogs of the $ROCH_2$ compounds disclosed and claimed in the subject application. The subject British patent discusses very little relating to the insecticidal activity of the compounds disclosed therein and it provides toxicity data on only two compounds. The data in the British patent indicates that a high concentration of these compounds is required in order to kill mites and also these compounds possess a high toxicity.

Therefore, the compounds of the subject application are distinguished not only by its excellent insecticidal action, but also by its greatly reduced mammalian toxicity.

The organophosphorus compounds of the subject invention can be characterized by the following structural formula:



wherein Z is a C_1 to C_6 alkyl—O—CH_2 group; X is either O or S; R_1 is a C_1 to C_6 alkyl group; R_2 is one selected from the group consisting of C_1 to C_{20} aliphatic, C_6 to C_{10} aromatic and heretocyclic moiety containing 3 to 8 carbon atoms.

Specific examples of those compounds covered by the above generic formula are as follows:

Compound No.

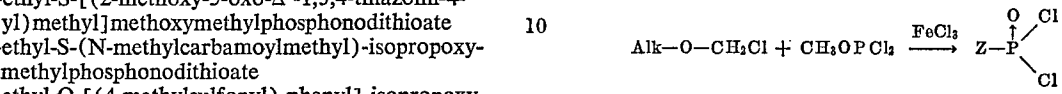
1 O-methyl-S-(p-chlorophenyl)-methoxymethylphosphonodithioate
2 O-methyl-O(1,2-dicarbethoxy)ethyl-methoxymethylphosphonothionate

3 O-methyl-O-2-pyrazinyl-methoxymethylphosphonothionate
4 O-methyl-S-(N-t.-butylcarbamoylmethyl)-methoxymethylphosphonodithioate
5 O-methyl-O-[4-(dimethyl-sulfamoyl)phenyl]-methoxymethylphosphonothionate
6 O-methyl-O-(4-cyanophenyl)-methoxymethylphosphonothionate
7 O-methyl-O-(4-nitrophenyl)-methoxymethylphosphonothionate
8 O-methyl-O-(2-chloro-4-nitro-phenyl)-methoxymethylphosphonothionate
9 O-methyl-S-(1,2-dicarbethoxy)ethyl-methoxymethylphosphonodithioate
10 O-ethyl-methoxymethylphosphonothionate O,O-diester with 4,4'-thiodiphenol
11 O-ethyl-O-(4-nitrophenyl)-methoxymethylphosphonothionate
12 O-ethyl-O[4(dimethylsulfamoyl)-phenyl]-methoxymethylphosphonothionate
13 O-ethyl-S-[4-oxo-(1,2,3-benzotriazine-3(4H)yl)-methyl]-methoxymethylphosphonodithioate
14 O-ethyl-S-(N-isopropylcarbamoylmethyl)-methoxymethylphosphonodithioate
15 O-ethyl-S-(N-methylcarbamoyloxymethyl)-methoxymethylphosphonodithioate
16 O-ethyl-O(2,3,5-trichloro-6-pyridyl)-methoxymethylphosphonothionate
17 O-ethyl-S-(4-nitrophenyl)-methoxymethylphosphonodithioate
18 O-ethyl-S-(1,2-dicarbomethoxy)ethyl-methoxymethylphosphonodithioate
19 O-ethyl-S-(1,2-dicarbethoxy)ethyl-methoxymethylphosphonodithioate
20 O,O'-diethyl-S,S'-methylene-bis(methoxymethylphosphonodithioate)
21 ethyl-(4-nitrophenyl)-methoxymethylphosphonate
22 ethyl-[4(N,N-dimethylsulfamoyl)phenyl]-methoxymethylphosphonate
23 ethyl-(4-cyanophenyl)-methoxymethylphosphonate
24 ethyl-(1,2-dicarbethoxy)-ethyl-methoxymethylphosphonate
25 O-ethyl-S-(1,2-dicarbethoxy)ethyl-methoxymethylphosphonothionate
26 O-ethyl-O-(4-nitrophenyl)-ethoxymethylphosphonothioate
27 O-ethyl-O-(4-cyanophenyl)ethoxymethylphosphonothionate
28 O-ethyl-O-(3-methyl-4-methylthio)-phenyl-ethoxymethylphosphonothionate
29 ethyl-(4-nitrophenyl)-ethoxymethylphosphonate
30 ethyl-(4-cyanophenyl)-isopropoxymethylphosphonate
31 ethyl-(1,2-dicarbethoxy)ethyl-isopropoxymethylphosphonate
32 O-ethyl-S[(6-chloro-2-oxo-3-benzoxazolinyl)methyl]-isopropoxymethylphosphonothionate
33 O-ethyl-S(1,2-dicarbethoxy)ethyl-isopropoxymethylphosphonodithioate
34 O-ethyl-S-(methylthiomethyl)-isopropoxymethylphosphonodithioate
35 O-ethyl-S-(4-chlorophenylthio)methylisopropoxymethylphosphonodithioate
36 O,O'-diethyl-S,S'-methylene-bis(isopropoxymethylphosphonodithioate)
37 O-ethyl-O-(2,3,5-trichloro-6-pyridyl)-isopropoxymethylphosphonothionate
38 O-ethyl-S-(4-cyanophenyl)-isopropoxymethylphosphonodithioate
39 O-ethyl-S-(4-chlorophenyl)-isopropoxymethylphosphonodithioate

40 O-ethyl-S-phenyl-isopropoxymethylphosphonodithioate
41 O-ethyl-S-(phthalimidomethyl)-isopropoxymethylphosphonodithioate
42 O-ethyl-S-[(6-chloro-2-oxo-3-benzoxazolinyl)methyl]-isopropoxymethylphosphonodithioate
43 O-ethyl-S-[4-oxo-1,2,3-benzotriazine-3(4H)-ylmethyl]-isopropoxymethylphosphonodithioate
44 O-ethyl-S-[(2-methoxy-5-oxo-Δ^2-1,3,4-thiazolin-4-yl)methyl]methoxymethylphosphonodithioate
45 O-ethyl-S-(N-methylcarbamoylmethyl)-isopropoxymethylphosphonodithioate
46 O-ethyl-O-[(4-methylsulfonyl)-phenyl]-isopropoxymethylphosphonothionate
47 O-ethyl-O-[(N,N-dimethylsulfamoyl)phenyl]-isopropoxymethylphosphonothionate
48 O-ethyl-O-(4-cyanophenyl)-isopropoxymethylphosphonothionate
49 O-ethyl-O-[(4-N,N-dimethylcarbamoyl)-phenyl]-isopropoxymethylphosphonothionate
50 O-ethyl-O-(4-carbomethoxyphenyl)-isopropoxymethylphosphonothionate
51 O-ethyl-O-[(3-trifluoromethyl)-phenyl]-isopropoxymethylphosphonothionate
52 O-ethyl-O-(2,4,5-trichlorophenyl)-isopropoxymethylphosphonothionate
53 O-ethyl-O-(3-chlorophenyl)-isopropoxymethylphosphonothionate
54 O-ethyl-O[(3-methyl-4-methylthio)-phenyl]-isopropoxymethylphosphonothionate
55 O-ethyl-O-(4-nitrophenyl)-isopropoxymethylphosphonothionate
56 O-ethyl-O-(3-methyl-4-nitrophenyl)-isopropoxymethylphosphonothionate
57 O-ethyl-S-(N-methylcarbamoyl)methyl-isopropoxymethylphosphonothiolate
58 O-ethyl-S-(N-isopropylcarbamoyl)methyl-isopropoxymethylphosphonodithioate
59 O-ethyl-S-(4-chlorophenylthiomethyl)-isopropoxymethylphosphonodithioate
60 O-ethyl-O-(4-nitrophenyl)-isobutoxymethylphosphonothionate
61 O-ethyl-O-[(4-N,N-dimethylsulfamoyl)-phenyl]-isobutoxymethylphosphonothionate
62 O-ethyl-O-(4-cyanophenyl)-isobutoxymethylphosphonothionate
63 O-ethyl-O-(3-methyl-4-nitrophenyl)-methoxymethylphosphonothionate
64 O-ethyl-S-phenyl-methoxymethylphosphonodithioate
65 O-ethyl-O-(2,4,5-trichlorophenyl)-methoxymethylphosphonothionate
66 O-ethyl-O-[(3-methyl-4-methylthio)-phenyl]-methoxymethylphosphonothionate
67 O-ethyl-S-(4-chlorophenyl)-methoxymethylphosphonodithioate
68 O-ethyl-S-(4-nitrophenyl)-methoxymethylphosphonothiolate
69 O-ethyl-S-(4-methylphenyl)-methoxymethylphosphonodithioate
70 O-ethyl-O-(2,4-dichlorophenyl)-methoxymethylphosphonothionate
71 O-ethyl-S-(phthalimidomethyl)-methoxymethylphosphonodithioate
72 O-ethyl-O-(4-chlorophenyl)-methoxymethylphosphonothionate
73 O-ethyl-O-(4-cyanophenyl)-methoxymethylphosphonothionate
74 O-ethyl-O-(4-methyl-2-oxo-2H-1-benzopyran-7-yl)-methoxymethylphosphonothionate
75 O-ethyl-S-(methylthiomethyl)-methoxymethylphosphonodithioate
76 O,O'-diethyl-S,S'-(oxydimethylene)-bis(methoxymethylphosphonodithioate)
77 O-ethyl-O-(2,4-dichlorophenoxymethyl)-methoxymethylphosphonothionate

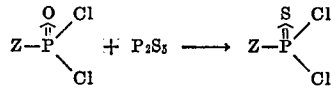
78 O-(4-nitrophenyl)-S-ethyl-methoxymethylphosphonodithioate
79 O-[(4-N,N-dimethylsulfamoyl)-phenyl]-S-ethyl-methoxymethylphosphonodithioate
80 O-(4-cyanophenyl)-S-ethyl-methoxymethylphosphonodithioate.

The synthesis of these compounds can be represented by the following schematic equations:

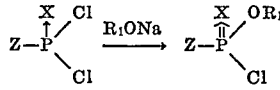


This reaction is described in Kwiatek et al. U.S. 2,882,313 and in Chemical Abstracts 53, 16965 (1959).

Step 2:

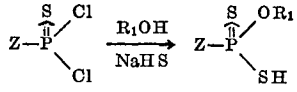


This reaction is described in the following article: E. Uhing et al., JACS, 83, 2299 (1961).



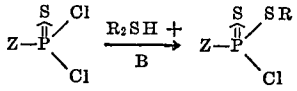
This reaction is carried out according to the methods and examples described by F. W. Hoffman et al. [(JACS, 80, 3945 (1958)] for phosphonate analogs of the subject intermediates. Therefore, the subject intermediates can be prepared according to these procedures described in this article and there is no need to go into any further detail at this time.

Another class of intermediates can be prepared according to the following schematic equation:

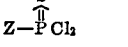


The preparation of these intermediates (O-alkylalkoxymethylphosphonodithioic acids) was carried out by using the method described by Szabo and Mann (JAFC, 17, 863 (1969).

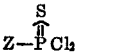
A still further class of intermediates were prepared according to the following schematic equation:



In this reaction from 1 to 2 moles of the reactant

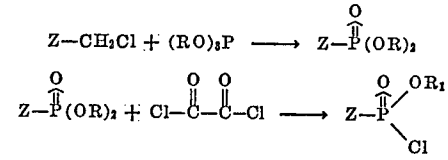


(alkoxymethylphosphonodichloridothioate) preferably, at least 1.5 moles are used for each mole of R_2SH and Base. The temperature of the reaction is preferably maintained between −5 and 20° C. The mixture of R_2SH and Base is gradually added to the



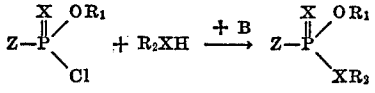
in inert solvent such as chloroform, methylene chloride, benzene toluene, ether, and the like.

A still further class of intermediates can be prepared according to the following schematic reactions.



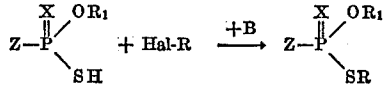
This reaction is described in an article entitled: Z. Pelchovica, Jr., Journal of the Chemical Society, 1961, 238.

Any of these intermediates can then be reacted with either a mercaptan or an alcohol in the presence of a base. The reaction is described for instance in the publication entitled: Houben-Weyl, "Methoden der Organischen Chemie," Parts 1 and 2, 1963; 1964.



This reaction is also described in the above-identified reference.

An alternative way to the formation of the end products is to react the alkoxyphosphoric, thiophosphoric or dithiophosphoric acids with a suitable halide according to the following schematic equation.



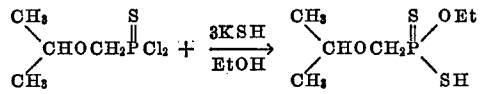
This reaction is also described in the above-identified reference.

The following examples are set forth in order to further set out the novel features of the subject invention.

TABLE I.—O-ALKYL-ALKOXYMETHYLPHOSPHONOTHIOLOTHIONIC ACIDS

Compound	Boiling point			P31 n.m.r., p.p.m.	Analysis								Yield, percent
					Calculated				Found				
	Degrees	Millimeters	n_D^{25}		C	H	P	S	C	H	P	S	
O-ethyl-methoxymethylphosphonothiolothionic acid	72-77	0.5	1.5333	−92.9	25.8	5.9	16.6	34.5	26.0	5.9	16.5	34.4	77
O-methyl-methoxymethylphosphonothiolothionic acid	63-66	0.3	1.5489	−96.2	21.0	5.3	18.0	37.3	20.9	5.4	18.3	36.9	35
O-ethyl-isopropoxymethylphosphonothiolothionic acid	74-80	0.1	1.5127	−94.2	33.8	7.1	14.5	30.1	33.6	7.1	14.7	30.1	58

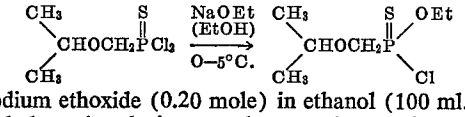
Example 1.—Preparation of ethyl isopropoxymethylphosphonothiolothionic acid



Isopropoxymethylphosphonothioic dichloride (35.2 g., 0.17 mole) was added dropwise during thirty minutes to a stirred solution of sodium hydrosulfide (0.51 mole) in ethanol (295 ml.) at −9 to −2° (Dry Ice-acetone cooling). The reaction mixture was evaporated at 50°/20 mm. for 20 minutes to yield a viscous opaque liquid. Water (130 ml.) was added to the liquid to yield a cloudy, yellow solution which was cooled to 10° by the addition of ice. Concentrated hydrochloric acid (20 ml.) was added to the stirred solution at 0–10°. The resulting mixture was extracted with methylene chloride (3× 200 ml.). The organic phase was dried with anhydrous magnesium sulfate, filtered, and the filtrate was evaporated at 40°/20 mm. to yield a yellow liquid, 34.6 g. The liquid was fractionated through a Vigreux column (8") to yield the product. The infrared spectrum of the product had peaks at 3100 cm.$^{-1}$ (aliphatic C—H), 2550 cm.$^{-1}$ (S—H), 1090 cm.$^{-1}$ (C—O—C), and 1040 cm.$^{-1}$, 960 cm.$^{-1}$ (P—O—C).

The following O - alkyl-alkoxymethylphosphonothiolothionic acids were prepared in the same manner as described hereinabove.

Example 2.—Preparation of ethyl isopropoxymethylphosphonochloridothionate



Sodium ethoxide (0.20 mole) in ethanol (100 ml.) was added dropwise during one hour and ten minutes to a stirred solution of isopropoxymethylphosphonothioic dichloride (39.9 g., 0.19 mole) in benzene (200 ml. at 2–4° in a nitrogen atmosphere. The reaction mixture was warmed to 26° during ten minutes, washed with water (3× 250 ml.), and dried over anhydrous magnesium sulfate. The mixture was filtered, and the filtrate was rotary evaporated at 45°/20 mm. to yield a colorless oil, 41 g. The oil was distilled through a 12" Vigreux to yield the product.

The gas chromatogram of the product (column, SE-30; temp. 110°) had a peak at 3.6 min. (area, 95%) and peaks at 2.2 min. (area, 1%) and 5.0 min. (area, 4%). The infrared spectrum of the product had peaks 1100 cm.$^{-1}$ (C—O—C), and 1040 cm.$^{-1}$, 970 cm.$^{-1}$

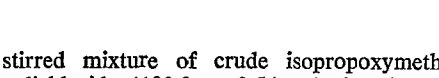
(P—O—C)

In like manner the following O-ethyl alkoxymethylphosphonochloridothioates were prepared:

TABLE II.—O-ETHYL ALKOXYMETHYLPHOSPHONO CHLORIDOTHIOATES

Compound	Boiling point			P31 n.m.r., p.p.m.	Analysis										Percent purity by G.C.	Yield, percent
					Calculated					Found						
	Degrees	Millimeters	n_D^{25}		C	H	Cl	P	S	C	H	Cl	P	S		
O-ethylmethoxymethylphosphono chlorodithioates	100.5-103.5	16	1.4952	−92.9	25.5	5.4	18.8	16.4	17.0	25.7	5.4	18.8	16.3	17.3	98	79
O-ethylisopropoxymethylphosphono chlorodithioates	61-63	0.1	1.4825	−93.4	33.4	6.5	16.4	14.3	14.8	33.6	6.5	16.3	14.3	14.9	95	61
O-ethylisobutoxymethylphosphono chlorodithioates	54.5-57	0.13	1.4781	−93.0			15.4					15.3			95	65

Example 3.—Preparation of isopropoxymethylphosphonothoic dichloride



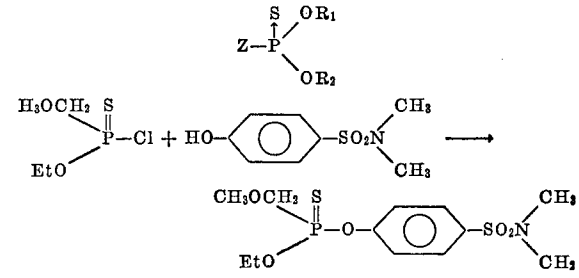
A stirred mixture of crude isopropoxymethylphosphonic dichloride (103.3 g., 0.54 m.),phosphorus pentasulfide (P_4S_{10}) (26.3 g., 0.05 m.) and thiophosphoryl chloride (186 ml.) was heated under nitrogen during five hours to 110° by means of an oil bath. The mixture was heated at 110–115° for five hours. The reaction mixture was cooled to room temperature, and was diluted with 2× 300 ml. of n-hexane to yield an insoluble solid. The mixture was filtered and the solid was washed with hexane The filtrate was washed quickly with water (350 ml.), dried over anhydrous magnesium sulfate, filtered, and rotary evaporated at 50°/20 mm. for two hours to yield a yellow liquid residue, 170 g. The liquid was fractionated with a 12" Vigreux column to yield the product. The gas chromatogram of the product (column, SE-30; temp. 85°), had a peak at 3.8 min. (area, >98%) followed by a shoulder (area <2%) at 5.2 min. The infrared spectrum of the product had peaks at 2990 cm.$^{-1}$ (aliphatic C—H) and 1090 cm.$^{-1}$ (C—O—C).

In like manner, the following alkoxymethylphosphonothioic dichlorides were prepared:

TABLE III.—ALKOXYMETHYLPHOSPHONOTHIOIC DICHLORIDES

Compound	Boiling point		n_D^{25}	P^{31} n.m.r., p.p.m.	Analysis										Yield, percent
					Calculated					Found					
	Degrees	Millimeters			C	H	D	P	S	C	H	D	P	S	
Methoxymethylphosphonothioic dichloride	83–85	----------	1.5408	−81.9	13.4	2.8	39.5	17.3	17.9	13.4	2.9	39.3	17.3	18.3	44
Ethoxymethylphosphonothioic dichloride	88.5–90	14	1.5261	−80.4	----------				16.6	----------				17.3	35
Isopropoxymethylphosphonothioic dichloride	87.5–94.5	14	1.5146	−83.0	23.2	4.4	34.2	15.0	15.5	23.4	4.5	34.0	15.0	15.7	40
Isobutoxymethylphosphonothioic dichloride	44.5–47	0.13	1.5084	−81.5	27.2	5.0	32.2	------	14.5	27.4	4.9	33.0	------	15.0	33

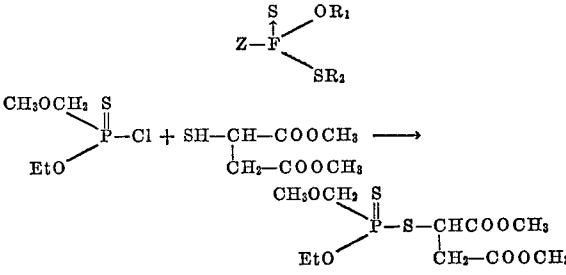
Example 4.—Preparation of ethyl-methoxymethylphosphonochloridothionate with N,N-dimethyl-p-hydroxy-benzenesulfonamide



Ethyl-methoxymethylphosphonochloridothionate (2.84 g., 15 mmoles) was added all at once to a solution of N,N-dimethyl-p-hydroxybenzenesulfonamide (3.01 g., 15 mmoles) and triethylamine (1.71 g., 17 mmoles) in acetone (30 ml.). A white solid started to separate after a few minutes. The reaction mixture was heated under reflux for 2 hours and 15 minutes. The mixture was cooled, and filtered to yield a white solid, triethylamine hydrochloride (1.73 g., 84% yield). The filtrate was evaporated at 40°/20 mm. to yield an amber oil. A benzene solution of the oil (50 ml.) was washed with water (50 ml.) and was dried over magnesium sulfate. The mixture was filtered and evaporated at 50°/20 mm. and at 25°/0.1 mm. to yield the product, a yellow oil, 4.8 g., 91% yield (n_D^{25} 1.5363).

Analysis. — Calc'd for $C_{12}H_{20}NO_5PS_2$ (percent): C=40.9; H=5.8; N=4.0. Found (percent): C=41.0; H=6.1; N=4.1. The infrared spectrum of the product had peaks of 1340 cm.$^{-1}$ and 1150 cm.$^{-1}$ (—SO_2—) and at 1100 cm.$^{-1}$ and 1020 cm.$^{-1}$ (P—O—C). The product had one peak in the P^{31} n.m.r. spectrum at −86.5 p.p.m. (H_3PO_4).

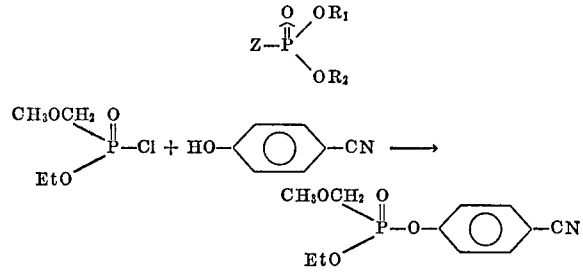
Example 5.—Preparation of ethyl-methoxymethylphosphonochloridothionate with dimethyl-mercaptosuccinate



A solution of triethylamine (2.35 g., 23 mmoles) and dimethyl-mercaptosuccinate (3.78 g., 21 mmoles) in benzene (20 ml.) was added dropwise to a stirred solution of ethylmethoxymethylphosphonochloridothionate (4.02 g., 21 mmoles) in benzene. A white solid started separating immediately. The reaction mixture was heated under reflux for one hour. The mixture was allowed to cool to room temperature and filtered to yield a solid, triethylamine hydrochloride (2.56 g., 86% yield). The filtrate was washed with water (100 ml.) and the organic phase was dried over magnesium sulfate. The mixture was filtered, and was evaporated at 50°/20 mm. and then at 25/0.1 mm. to yield the product, a pale yellow oil, 6.1 g., 86% yield (n_D^{17} 1.5111). The oil had one major peak (96% by area) in the gas chromatogram at 7.2 min. (T=185°, 5% SE–30 on Chrom. W., 5 ft. column, N_2=16 p.s.i.).

Analysis.—Calc'd. for $C_{10}H_{19}O_6PS_2$ (percent): C=36.4; H=5.8; P=9.4; S=19.4. Found (percent): C=36.4; H=6.0; P=9.7; S=19.7. The infrared spectrum of the product had a peak at 1740 cm.$^{-1}$ (C=O) and peaks at 1100 cm.$^{-1}$ and 1020 cm.$^{-1}$ (P—O—C). The product had one peak in the P^{31} n.m.r. spectrum at −98.3 p.p.m. (H_3PO_4).

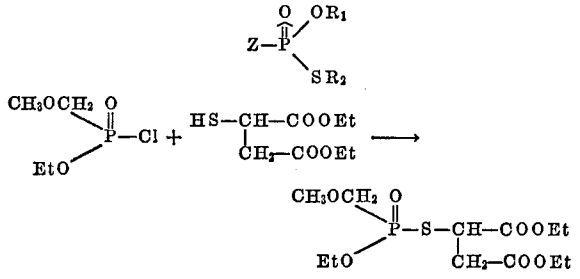
Example 6.—Preparation of ethyl methoxymethylphosphonochloride with p-cyanophenol



A solution of ethyl-methoxymethylphosphonochloridate (3.45 g., 20 mmoles) in acetone (10 ml.) was added all at once to a solution of triethylamine (2.12 g., 21 mmoles and p-cyanophenol (2.38 g., 20 mmoles) in acetone (20 ml.). There was an exothermic reaction and a white solid separated. The mixture was heated under reflux for one-half hour and then allowed to stand overnight at room temperature. The mixture was filtered to yield a solid, triethylamine hydrochloride, 2.44 g., 89% yield. The filtrate was added to water (100 ml.). Salt was added to the resulting mixture and the mixture extracted with dichloromethane (100 ml.; 50 ml.). The organic phase was washed with 5% sodium carbonate solution (100 ml.) and water (3× 100 ml.) The organic phase was dried ($MgSO_4$), filtered and evaporated at 50°/20 mm. and then 50°/0.1 mm. to yield the product a pale yellow liquid, 4.6 g., 90% yield, n_D^{21} 1.5086. The product had one peak in the gas chromatogram at 2.8 min. (T=185°, 5% SE–30 on Chromosorb W., 5 ft. column, N_2=16 p.s.i.).

The infrared spectrum of the product had a peak at 2280 cm.$^{-1}$ (—CN) and peaks at 1120 cm.$^{-1}$ and 1040 cm.$^{-1}$ (P—O—C).

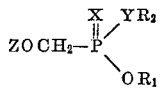
Example 7.—Preparation of ethyl methoxymethylphosphonochloride with diethyl-mercaptosuccinate



Ethyl-methoxymethylphosphonochloridate (3.45 g., 20 mmoles) in acetone (10 ml.) was added all at once to a solution of triethylamine (212 g., 21 mmoles) and diethylmercaptosuccinate (4.12 g., 20 mmoles) in acetone (20 ml.) immersed in a water bath. There was an immediate precipitate and an exothermic reaction. The mixture was heated under reflux for 20 minutes and then allowed to cool to room temperature. The mixture was filtered to yield a white solid, triethylamine hydrochloride, 2.56 g., 93% yield. The filtrate was poured into water (100 ml.). This mixture was extracted with dichloromethane. The organic phase was washed with 5% sodium carbonate solution (100 ml.), and water (200 ml.). The organic phase was dried ($MgSO_4$), filtered, and evaporated at 50°/20 mm. and 55°/0.1 mm. to yield the product, a yellow liquid, 5.4 g., 80% yield, n_D^{21} 1.4716. On standing, the product became cloudy with a small amount of solid. The cloudy oil was filtered to yield a clear yellow liquid. The gas chromatogram of the liquid had one peak at 5.7 min. (T=185°, 5% SE-30 on Chrom. W., 5 ft. column, N_2=16 p.s.i.). The infrared spectrum of the liquid had a peak at 1740 cm.$^{-1}$ (C=O) and peaks at 1120 cm.$^{-1}$ and 1040 cm.$^{-1}$ (P—O—C). The P^{31} n.m.r. had a major peak (>90%) at −45.9 p.p.m. (H_3PO_4).

Other compounds of this invention were prepared by methods given in Examples 4 to 7. The structure of these compounds were confirmed by infrared and NMR spectroscopy. They were also characterized by refractive indices which are listed in the following table:

TABLE IV



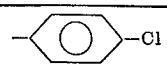
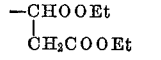
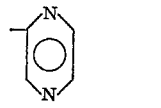
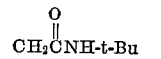
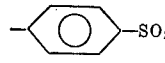
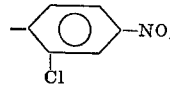
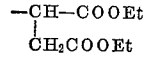
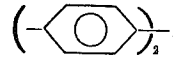
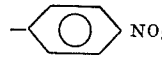
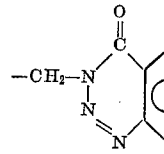
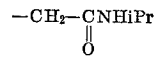
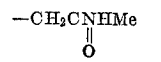
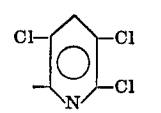
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3	Me	Me		S	O	1.5357
4	Me	Me		S	S	1.5337
5	Me	Me		S	O	1.5455
6	Me	Me		S	O	1.5515
7	Me	Me		S	O	1.5621
8	Me	Me		S	O	1.5697
9	Me	Me		S	S	1.5073
10[a]	Me	Et		S	O	1.5751
11	Me	Et		S	O	1.5537
12	Me	Et		S	O	1.5383
13	Me	Et		S	S	1.6176
14	Me	Et		S	S	1.5373
15	Me	Et		S	S	1.5492
16	Me	Et		S	O	1.5555

TABLE IV—Continued

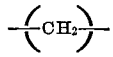
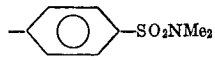
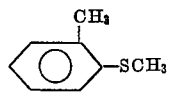
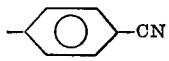
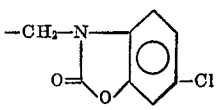
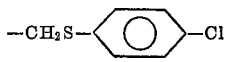
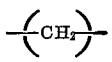
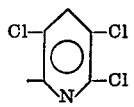
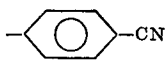
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19	Me	Et	$-CH(CH_2-COOEt)-COOEt$	S	S	1.4978
20 [a]	Me	Et		S	S	1.5485
21	Me	Et		O	O	1.5208
22	Me	Et		O	O	1.5130
23	Me	Et		O	O	1.5090
24	Me	Et	$-CH(CH_2-COOEt)-COOEt$	O	O	1.4402
25	Me	Et	$-CH(CH_2-COOEt)-COOEt$	O	S	1.4720
26	Et	Et		S	O	1.5421
27	Et	Et		S	O	1.5325
28	Et	Et		S	O	1.5465
29	Et	Et		O	O	1.5173
30	i-Pr	Et		O	O	1.5007
31	i-Pr	Et	$-CH(CH_2COOEt)-COOEt$	O	O	1.4411
32	i-Pr	Et		S	O	1.5364
33	i-Pr	Et	$-CH(CH_2-COOEt)-COOEt$	S	S	1.4945
34	i-Pr	Et	$-CH_2-SCH_3$	S	S	1.5317
35	i-Pr	Et		S	S	1.5858
36 [a]	i-Pr	Et		S	S	1.5405
37	i-Pr	Et		S	O	1.5401
38	i-Pr	Et		S	S	1.5729
39	i-Pr	Et		S	S	1.5677
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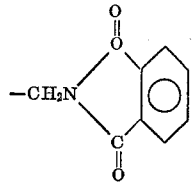
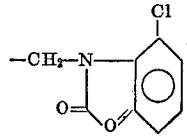
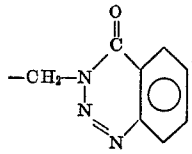
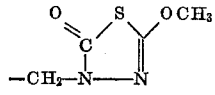
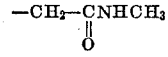
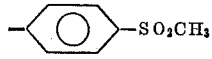
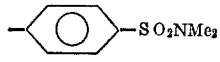
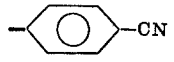
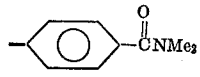
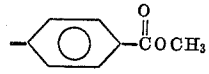
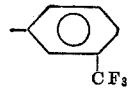
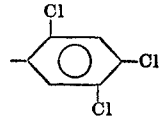
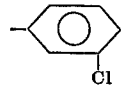
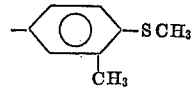
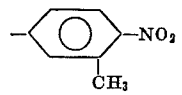
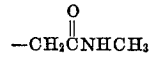
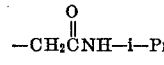
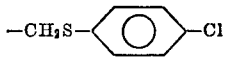
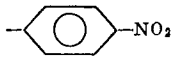
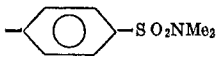
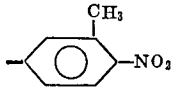
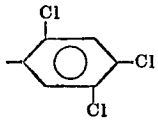
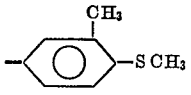
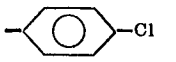
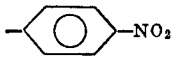
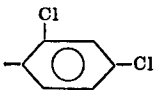
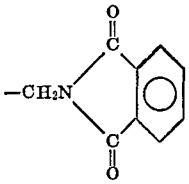
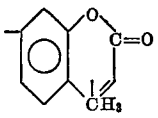
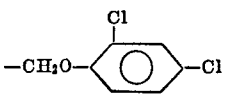
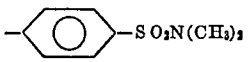
Compound No.	Z	R_1	R_2	X	Y	n_D^{20}
41	i-Pr	Et		S	S	1.5801
42	i-Pr	Et		S	S	1.5764
43	i-Pr	Et		S	S	1.5971
44	i-Pr	Et		S	S	1.5664
45	i-Pr	Et		S	S	1.5332
46	i-Pr	Et		S	O	1.5315
47	i-Pr	Et		S	O	1.5298
48	i-Pr	Et		S	O	1.5246
49	i-Pr	Et		S	O	1.5294
50	i-Pr	Et		S	O	1.5183
51	i-Pr	Et		S	O	1.4759
52	i-Pr	Et		S	O	1.5407
53	i-Pr	Et		S	O	1.5176
54	i-Pr	Et		S	O	1.5445
55	i-Pr	Et		S	O	1.5374
56	i-Pr	Et		S	O	1.5355
57	i-Pr	Et		O	S	1.4873
58	i-Pr	Et		S	S	1.5199

TABLE IV—Continued

Compound No.	Z	R_1	R_2	X	Y	n_D^{20}
59	i-Pr	Et		S	S	1.5858
60	iBu	Et		S	O	1.5314
61	iBu	Et		S	O	1.5222
62	iBu	Et		S	O	1.5216
63	Me	Et		S	O	1.5530
64	Me	Et		S	S	1.5839
65	Me	Et		S	O	1.5559
66	Me	Et		S	O	1.5636
67	Me	Et		S	S	1.5940
68	Me	Et		S	O	1.5523
69	Me	Et		S	S	1.5827
70	Me	Et		S	O	1.5490
71	Me	Et		S	S	[1] 78
72	Me	Et		S	O	1.5333
73	Me	Et		S	O	1.5385
74	Me	Et		S	O	[1] 81
75	Me	Et	$-CH_2SCH_3$	S	S	1.5592
76 [a]	Me	Et	$-CH_2OCH_2-$	S	S	1.5614
77	Me	Et		S	O	1.5850
78	Me		Et	S	S	1.5996
79	Me		Et	S	S	1.5766
80	Me		Et	S	S	1.5890

[1] Degree centigrade.

The compounds of the invention have general insecticidal properties. Insecticidal compositions of the invention are prepared by admixing one or more of the active ingredients defined heretofore, in insecticidally effective amounts with a conditioning agent of the kind used and referred to in the art as a pest control adjuvant or modifier to provide formulations adapted for ready and efficient application to the soil using conventional applicator equipment.

Thus, the insecticidal compositions or formulations are prepared in the form of solids or liquids. Solid compositions are preferably in the form of granulars or dusts.

The compositions can be compounded to give homogeneous free-flowing dusts by admixing the active compound or compounds with finely divided solids preferably talc, natural clays, pyrophyllite, diatomaceous earth, or flours such as walnut shell, wheat, redwood, soya bean, and cottonseed flours. Other inert solid conditioning agents or carriers of the kind conventionally employed in preparing pest control compositions in powdered from can be used.

Granulars can be compounded by absorbing the compound in liquid form onto a preformed granular diluent. Such diluents as natural clays, pyrophyllite, diatomaceous earth, flours such as walnut shell, as well as granular sand can be employed.

In addition, granulars can also be compounded by admixing the active ingredient with one of the powdered diluents described hereinabove, followed by the step of either pelleting or extruding the mixture.

Liquid compositions of the invention are prepared in the usual way by admixing one or more of the active ingredients with a suitable liquid diluent medium. In the cases where the compounds are liquids, they may be sprayed in ultra low volume as such. With certain solvents, such as alkylated naphthalene or other aromatic petroleum solvents, dimethyl formamide, cycloketone, relatively high up to about 50% by weight or more concentration of the active ingredient can be obtained in solution.

The insecticidal compositions of the invention whether in the form of dusts or liquids, preferably also include a surface-active agent sometimes referred to in the art as a wetting, dispersing, or emulsifying agent. These agents, which will be referred to hereinafter more simply as surface-active dispersing agents, cause the compositions to be easily dispersed in water to give aqueous sprays which, for the most part, constitute a desirable composition for application.

The surface-active dispersing agents employed can be of the anionic, cationic, or nonionic type and include, for example, sodium and potassium oleate, the amine salts of oleic acid, such as morpholine and dimethylamine oleates, the sulfonated animal and vegetable oils, such as sulfonated fish and castor oils, sulfonated petroleum oils, sulfonated acyclic hydrocarbons, sodium salt of lignin sulfonic acid (goulac), alkylnaphthalene sodium sulfonate, sodium salts of sulfonated condensation products of naphthalene and formaldehyde, sodium lauryl sulfate, disodium monolauryl phosphate, sorbitol laurate, pentaerythritol monostearate, glycerol monostearate, diglycol oleate, polyethylene oxides, ethylene oxide condensation products with stearyl alcohol and alkylphenol, polyvinyl alcohols, salts, such as the acetate of polyamines from reductive amination of ethylene/carbon monoxide polymers, laurylamine hydrochloride, lauryl-pyridinium bromide, stearyl trimethylammonium bromide, cetyl-dimethylbenzyl ammonium chloride, lauryldimethylamine oxide, and the like. Generally, the surface-active agent will not compirse more than about 5 to 15% by weight of the composition, and in certain compositions the percentage will be 1% or less. Usually, the minimum lower concentration will be 0.1%.

The insecticidal compositions are applied either as a spray, granular or a dust to the locus or area to be protected from undesirable insects. Such application can be made directly upon the locus or area and the insects thereon during the period of infestation in order to destroy the insects, but preferably, the application is made in advance of an anticipated insect infestation to prevent such infestation. Thus, the compositions can be applied as aqueous foliar sprays but can also be applied as sprays directly to the surface of the soil. Alternatively, the dry powdered compositions can be dusted directly on the plants or on the soil.

The active compound is, of course, applied in an amount sufficient to exert the desired insecticidal action. The amount of the active compound present in the compositions as actually applied for destroying or preventing infestation by the insects will vary with the manner of application, the particular insect for which control is sought, the purpose for which the application is being made, and like variables. In general, the insecticidal compositions as applied in the form of a spray, dust or granular, will contain from about 0.1% to 100% by weight of the active compound.

The term "carrier" or "diluent" as used herein means a material, which can be inorganic or organic and synthetic or of natural origin, with which the active ingredient is mixed or formulated to facilitate its storage, transport, and handling and application to the plants to be treated. The carrier is preferably biologically and chemically inert and, as used, can be a solid or fluid. When solid carriers are used, they are preferably particulate, granular, or pelleted; however, other shapes and sizes of solid carrier can be employed as well. Such preferable solid carriers can be natural occurring minerals—although subsequently subjected to grinding, sieving, purification, and/or other treatments—including, for example, gypsum; tripolite; diatomaceous earth, mineral silicates such as mica, vermiculite, talc, and pyrophyllite; clays of the montmorillonite, kaolinite, or attapulgite groups; calcium or magnesium limes, or calcite and dolomite; etc. Carriers produced synthetically, as for example, synthetic hydrated silica oxides and synthetic calcium silicates can also be used, and many proprietary products of this type are available commercially. The carrier can also be an elemental substance such as sulfur or carbon, preferably an activated carbon. If the carrier possesses intrinsic catalytic activity such that it would decompose the active ingredient, it is advantageous to incorporate a stabilizing agent, as for example, polyglycols such as diethylene glycol, to neutralize this activity and thereby prevent possible decomposition of the present compounds.

For some purposes, a resinous or waxy carrier can be used, preefrably one which is solvent soluble or thermoplastic, including fusible. Examples of such carriers are natural or synthetic resins such as a coumarone resin, rosin, copal, shellac, dammar, polyvinyl chloride, styrene polymers and copolymers, a solid grade of polychlorophenol such as is available under the registered trademark "Aroclor," a bitumen, an asphaltite, a wax for example, beeswax or a mineral wax such as paraffin wax or montan wax, or a chlorinated mineral wax, or a microcrystalline wax such as those available under the registered trademark "Mikrovan Wax." Compositions comprising such resinous or waxy carriers are preferably in granular or pelleted form.

Fluid carriers can be liquids, as for example, water, or an organic fluid, including a liquefied normally vaporous or gaseous material, or a vaporous or gaseous material, and can be solvents or nonsolvents for the active material. For example, the horticultural petroleum spray oils boiling in the range of from about 275° to about 575° F., or boiling in the range of about 575° to about 1,000° F. and having an unsulfonatable residue of at least about 75% and preferably of at least about 90%, or mixtures of these two types of oil, are particularly suitable liquid carriers.

The carrier can be mixed or formulated with the active material during its manufacture or at any stage subsequently. The carrier can be mixed or formulated with the active material in any proportion depending on the nature of the carrier. One or more carriers, moreover, can be used in combination.

The compositions of this invention can be concentates, suitable for storage or transport and containing, for example, from about 5 to about 90% by weight of the active ingredient, preferably from about 20 to about 80 wt. percent. These concentrates can be diluted with the same or different carrier to a concentration suitable for application. The compositions of this invention may also be dilute compositions suitable for application. In general, concentrations of about 0.1 to about 10% by weight, of active material based on the total weight of the compositions are satisfactory, although lower and higher concentrations can be applied if necessary.

The compositions of this invention can also be formulated as dusts. These comprise an intimate admixture of the active ingredient and a finely powdered solid carrier such as aforedescribed. The powdered carriers can be oil treated to improve adhesion to the surface to which they are applied. These dusts can be concentrates, in which case a highly sorptive carrier is preferably used. These require dilution with the same or a different finely powdered carrier, which can be of lower sorptive capacity, to a concentration suitable for application.

The compositions of the invention can be formulated as wettable powders comprising a major proportion of the active ingredient mixed with a dispersing, i.e., deflocculating or suspending agent, and if desired, a finely divided solid carrier and/or a wetting agent. The active ingredient can be in particulate form or adsorbed on the carrier and preferably constitutes at least about 10%, more preferably at least about 25% by weight of the composition. The concentration of the dispersing agent should in general be between about 0.5 and about 5% by weight of the total composition, although larger or smaller amounts can be used if desired.

The dispersing agent used in the composition of this invention can be any substance having definite dispersing, i.e., deflocculating or suspending, properties as distinct from wetting properties, although these substances can also possess wetting properties as well.

The dispersant or dispersing agent used can be protective colloids such as gelatin, glue, casein, gums, or a synthetic polymeric material such as polyvinyl alcohol and methyl cellulose. Preferably, however, the dispersants or dispersing agents used are sodium or calcium salts of high molecular weight sulfonic acids, as for example, the sodium or calcium salts or lignin sulfonic acids derived from sulfite cellulose waste liquors. The calcium or sodium salts of condensed aryl sulfonic acid, for example, the products known as "Tamol 731," are also suitable.

The wetting agents used can be nonionic type surfactants, as for example, the condensation products of fatty acids containing at least 12, preferably 16 to 20, carbon atoms in the molecule, or abietic acid or naphthenic acid obtained in the refining of petroleum lubricating oil fractions with alkylene oxides such as ethylene oxide or propylene oxide, or with both ethylene oxide and propylene oxide, as for example, the condensation product of oleic acid and ethylene oxide containing about 6 to 15 ethylene oxide units in the molecule. Other nonionic wetting agents like polyalkylene oxide polymers, commercially known as "Pluronics" can be used. Partial esters of the above acids with polyhydric alcohols such as glycerol, polyglycerol, sorbitol, or mannitol can also be used.

Suitable anionic wetting agents include the alkali metal salts, preferably sodium salts, of sulfuric acid esters or sulfonic acids containing at least 10 carbon atoms in a molecule, for example, the sodium secondary alkyl sulfates, dialkyl sodium sulfosuccinate available under the registered trademark "Teepol," sodium salts of sulfonated castor oil, sodium dodecyl benzene sulfonate.

Granulated or pelleted compositions comprising a suitable carrier having the active ingredient incorporated therein are also included in this invention. These can be prepared by impregnating a granular carrier with a solution of the inert ingredient or by granulating a mixture of a finely divided solid carrier and the active ingredient. The carrier used can consist of or contain a fertilizer or fertilizer mixture, as for example, a superphosphate.

The compositions of this invention can also be formulated as solutions of the active ingredient in an organic solvent or mixture of solvents, such as for example, alcohols; ketones, especially acetone; ethers, hydrocarbons, etc.

Where the toxicant itself is a liquid these materials can be sprayed on crops or insects without further dilution.

Petroleum hydrocarbon fractions used as solvents should preferably have a flash point above 73° F., an example of this being a refined aromatic extract of kerosene. Auxiliary solvents such as alcohols, ketones, and polyalkylene glycol ethers and esters can be used in conjunction with these petroleum solvents.

Compositions of the present invention can also be formulated as emulsifiable concentrates which are concentrated solutions or dispersion of the active ingredient in an organic liquid, preferably a water-insoluble organic liquid, containing an added emulsifying agent. These concentrates can also contain a proportion of water, for example, up to about 50% by volume, based on the total composition, to facilitate subsequent dilution with water. Suitable organic liquids include, e.g., the above petroleum hydrocarbon fractions previously described. Higher concentrations may be prepared using polar cosolvents such as cyclohexanone or dimethylformamide.

The emulsifying agent can be of the type producing water-in-oil type emulsions which are suitable for application by low volume spraying or an emulsifier of the type producing oil-in-water emulsions can be used, producing concentrates which can be diluted with relatively large volumes of water for application by high volume spraying or relatively small volumes of water for low volume spraying. In such emulsions, the active ingredient is preferably in a nonaqueous phase.

The present invention is further illustrated in greater detail by the following examples, but it is to be understood that the present invention in its broadest aspects is not necessarily limited in terms of the reactants or specific temperatures, residence times, separation techniques and other process conditions, etc.; or dosage level, exposure times, test species used, etc. by which the compounds and/or compositions described and claimed are prepared and/or used.

In the examples which follow, the compounds were treated in the greenhouse and in the laboratory to determine their biological activity.

The experimental compounds were tested as aqueous emulsions. These emulsions were prepared by dissolving the compound in acetone and dispersing it in distilled water with Triton X–100, an alkalaryl polyether alcohol derived by the reaction of i-octyl phenol with ethylene oxide, to give spray emulsions containing the desired concentration of the compound. These emulsions were then used in standard laboratory tests described below.

Mexican bean beetle: Bean leaves were dipped in the emulsion of the test chemical and allowed to dry. The individual treated leaves were placed in Petri dishes and five Mexican bean beetle larvae introduced into each of the two replicate dishes.

Mites, contact: Potted bean plants infested with the two-spotted spider mites were placed on a turntable and sprayed with a formulation of the test chemical. The

plants were held for seven days and the degree of mite control was rated after this period.

Mites, systemic: Bean plants were treated by applying 20 ml. of the formulated test chemical to the soil. The mites were transferred to the plants after 24 hours. The plants were held for seven more days and the degree of mite control rated.

Aphid, contact: Potted nasturtium plants infested with the bean aphids were placed on a turntable and sprayed with a formulation of the test chemical. The plants were held for two days and the degree of aphid control was rated.

Aphid, systemic: Nasturtium plants were treated by applying 20 ml. of the formulated test chemical to the soil. The mites were transferred to the plants after 24 hours. The plants were held for 48 additional hours and the degree of the Aphid control rated.

Southern army worm: Bean leaves were dipped in the emulsion of the test chemical of desired concentration and allowed to dry. The individual treated leaves were placed in Petri dishes and five southern army larvae introduced into each of the two replicate dishes. The plants were held for two days and the degree of control was rated.

Some of the compounds were also tested against other species of coleoptera family such as confused flour beetle and spider beetle, as well as adult Mexican bean beetles. They were also tested for their effectiveness to control German cockroaches and houseflies. Tests were also done to determine their ovicidal action. The compounds were found active in one or more of these tests.

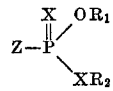
Representative data for a number of compounds demonstrating their insecticidal activity are presented in Table V.

TABLE V

Number	MBB	Mites		Aphids		SAW	HF
		Contact	Systemic	Contact	Systemic		
1	8	0	0	0	3	10	7
2	0	0	0	0	0	0	1
3	10	10	0	10	5	0	1
4	2	10	1	10	10	0	0
5	10	4	0	10	0	8	10
6	10	8	0	10	1	0	10
7	10	10	0	10	0	2	10
8	0	10	0	10	2	0	5
9	4	0	0	10	3	2	1
10	0	0	0	0	2	2	10
11	10	10	6	10	1	10	10
12	10	8	0	2	1	0	10
13	10	10	8	10	2	8	7
14	0	10	9	10	10	0	10
15	0	9	6	10	10	0	10
16	0	5	0	10	1	2	10
17	0	0	0	2	0	0	0
18	0	10	3	10	1	0	10
19	8	10	4	10	4	0	10
20	0	8	0	10	1	0	10
21	8	10	8	8	0	0	10
22	8	0	0	6	0	0	9
23	0	0	0	2	0	0	10
24	0	0	0	0	0	0	0
25	2	0	0	10	0	0	10
26	10	10	0	10	0	10	10
27	10	10	0	10	0	8	10
28	10	10	0	10	0	4	10
29	8	10	0	10	0	0	10
30	10	10	0	9	0	6	10
31	2	0	0	0	0	0	0
32	2	0	0	4	0	0	2
33	10	10	5	10	3	0	10
34	10	10	10	10	3	0	10
35	10	10	1	10	4	0	10
36	10	10	0	10	0	0	1
37	10	10	2	10	0	6	10
38	10	10	2	8	0	0	10
39	10	10	0	10	1	9	10
40	10	0	0	7	0	0	10
41	10	0	0	10	4	0	10
42	10	10	2	10	10	0	10
43	10	10	4	10	4	4	10
44	10	10	0	10	10	0	10
45	10	10	10	10	10	0	10
46	10	10	0	10	0	8	10
47	10	10	1	10	2	0	10
48	10	10	9	10	3	10	10
49	10	0	0	7	0	0	10
50	10	0	0	7	0	0	10
51	0	0	0	3	0	2	10
52	2	8	4	10	4	2	10
53	10	0	0	5	0	4	10
54	10	10	1	10	4	0	10
55	10	10	0	10	3	10	10
56	10	8	4	10	2	8	10
57	10	10	10	10	10	0	10
58	10	10	10	10	10	0	10
59	10	10	1	10	4	0	10
60	10	0	0	10	0	0	10
61	10	0	0	3	0	0	10
62	10	0	0	0	0	0	10
63	10	10	6	10	2	8	10
64	0	0	0	10	5.5	0	10
65	0	10	4	10	0	10	10
66	2	10	8	10	6	0	10
67	10	8	5	10	4	4	10
68	10	10	0	10	4	0	10
69	10	6	3	3	1	0	10
70	0	8	2	10	10	0	10
71	10	9	0	0	4	0	7
72	0	0	0	0	1	0	10
73	10	8	0	5	1	10	10
74	0	0	0	0	7	0	0
75	0	9	9	10	10	0	10
76	0	0	5	0	0	1	2
77	0	0	0	7	2	0	10
78	0	8	0	0	1	0	1
79	0	0	2	0	0	0	0
80	2	7	0	0	5	0	0

What is claimed is:

1. Compounds of the formula:



wherein Z is a C_1 to C_6 alkyl—O—CH_2 group; X is either O or S; R_1 is a C_1 to C_6 alkyl group; R_2 is phenyl substituted by chloro, nitro or lower alkyl.

2. A compound of claim 1 wherein R_2 is chloro substituted phenyl.

3. A compound according to claim 1, O-methyl-S-(p-chlorophenyl)-methoxymethylphosphonodithioate.

4. A compound according to claim 1, O-methyl-O-(4-nitrophenyl)-methoxymethylphosphonothionate.

5. A compound according to claim 1, O-methyl-O-(2-chloro - 4 - nitro-phenyl)-methoxymethylphosphonothionate.

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LEWIS GOTTS, Primary Examiner

R. L. RAYMOND, Assistant Examiner

U.S. Cl. X.R.

260—248 R, 251 P, 290 R, 307 D, 326 R, 928, 929, 940, 941, 942, 943, 944, 945, 948, 949, 951, 972, 973, 979; 424—200, 205, 206, 210, 211, 212, 216, 217