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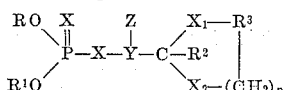
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CYCLIC MERCAPTALS

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5 Claims. (Cl. 260—327)

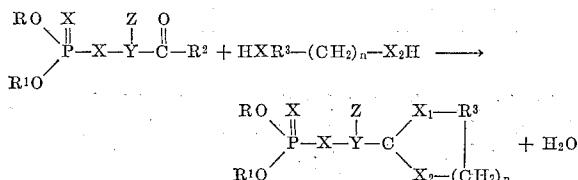
This invention is directed to a new class of phosphorus-containing cyclic mercaptals and acetals, their method of preparation and use as pesticides.

The new compounds of this invention may be represented by the following formula:



wherein R and R¹ are lower alkyl radicals, R² is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 5 carbon atoms, R³ is selected from the group consisting of methylene and carbonyl, n is an integer from 1 to 2; the groups represented by X are independently selected from the group consisting of oxygen and sulfur, and Y is selected from the group consisting of alkylene radicals having from 1 to 3 carbon atoms and phenylene; and Z is selected from the group consisting of hydrogen and carbethoxy. Suitable alkyl radicals for R and R¹ include methyl, ethyl, propyl, isopropyl, amyl, octyl, and the like.

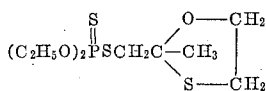
Preparation of the compounds of the present invention is accomplished by reacting a phosphorylated aldehyde or ketone with a glycol or mono- or dimercaptan, preferably in the presence of an acid catalyst. This reaction may be represented by the following equation:



wherein R, R¹, R³, X, X₁, X₂, Y, Z, and n are as described hereinbefore. A solvent such as benzene and ethyl ether may be used but is not strictly essential to the process. Among the suitable acid catalysts for the reaction are boron trifluoride etherate and gaseous HCl. The reaction may be carried out at temperatures between 0° C. and 100° C. but preferably between about 20° C. and 50° C. Normally, the reaction product will be washed to remove any side products and/or unreacted materials. An aqueous solution of sodium bisulfite will be used to remove unreacted phosphorylated aldehydes. To remove side products, the reaction mixture may be washed with a solution of sodium hydroxide and then dried with sodium sulfate or calcium chloride.

The following examples illustrate specific compounds prepared by the method of the present invention.

EXAMPLE 1

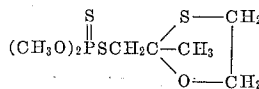


To 24.2 grams of CH₃C(O)—CH₂SP(S)(OC₂H₅)₂ in 8.8 grams of 2-mercapto ethanol was added 4 drops of (C₂H₅)₂O·BF₃. A slightly exothermic reaction was observed. The mixture was allowed to stir at a temperature of between 25 and 32° C. for 18 hours, after which time it was transferred to a separatory funnel and ex-

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tracted with 400 ml. of ether. The ether phase containing the product was then washed twice with 500 ml. portions of water and dried over sodium sulfate. After stripping the solvent off by heating the mixture to 50° C. at 1 mm. of Hg, the product was analyzed and found to contain 26.3 grams (87.0% yield) of 2-[O,O-diethyl phosphorodithio methyl]-2-methyl-1,3-oxathiolane, having an index of refraction N_D²⁵=1.5430 and the elemental analysis of 9.6% P and 32.3% S compared to 10.2% P and 31.8% S, theoretical.

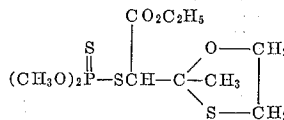
EXAMPLE 2



To 12.5 grams of (CH₃O)₂P(S)SCH₂C(O)CH₃ and 4.6 grams of 2-mercapto ethanol was added gaseous HCl. A vigorous exothermic reaction resulted and H₂O was observed to settle to the bottom of the reaction mixture. After 30 minutes, 100 ml. of benzene was added and the mixture was stirred for about 17 hours. The benzene was then stripped off by heating the mixture to 60° C. at 1 mm. of Hg to yield 15.5 grams (100% yield) of 2-(O,O-dimethyl dithiophosphoromethyl)-2-methyl-1,3-oxathiolane, having an index of refraction N_D²⁵=1.5598 and an analysis of 10.5% P and 37.7% S compared to 11.2% P and 35.2% S, theoretical.

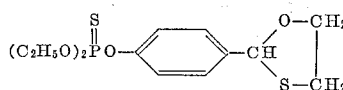
Using a procedure substantially in accordance with Examples 1 or 2, the following specific compounds were prepared.

EXAMPLE 3



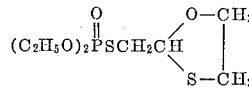
2-(O,O-dimethyl phosphorodithio-carbethoxy methyl)-2-methyl-1,3-oxathiolane; N_D²⁵=1.5334; yield 13.2 grams (75%); percent P=9.1 (9.0 theory); percent S=27.8 (27.8 theory).

EXAMPLE 4



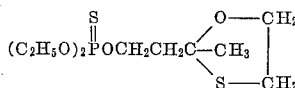
O,O-dimethyl-O-(4-oxo-phenyl)-phosphorothioate cyclic ethylene hemithioacetal; N_D²⁵=1.5520; yield=62 grams (93%); percent P=9.3 (9.3 theory); percent S=20.3 (19.2 theory).

EXAMPLE 5



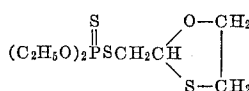
2-(O,O-diethyl phosphorothiomethyl)-1,3-oxathiolane; N_D²⁵=1.5268; yield=12.5 grams (46%); percent P=9.0 (11.4 theory); percent S=27.9 (23.6 theory).

EXAMPLE 6



2-(O,O-diethylphosphorothionocetyl)-2-methyl-1,3-oxathiolane; N_D²⁵=1.4975; yield=7.5 grams (86%); percent S=20.4 (21.4 theory).

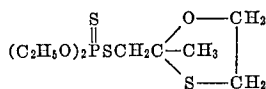
EXAMPLE 7



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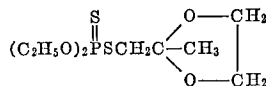
2-(O,O-diethylphosphorodithiomethyl) - 1,3 - oxathiolane; $N_D^{25}=1.5540$; yield=20.0 grams (94%); percent P=11.4 (10.8 theory); percent S=33.9 (33.4 theory).

EXAMPLE 8



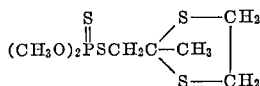
2-(O,O-diethylphosphorodithiomethyl) - 2-methyl - 1,3-oxathiolane; $N_D^{25}=1.5340$; yield=5.0 grams (32%); percent P=10.0 (9.8 theory); percent S=29.4 (30.3 theory).

EXAMPLE 9



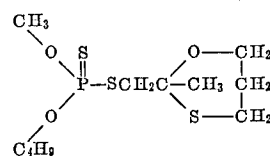
2-(O,O-diethylphosphorodithiomethyl) - 2-methyl - 1,3-dioxalane; $N_D^{25}=1.5083$; yield=25.0 grams (88%); percent P=11.9 (11.0 theory); percent S=22.9 (22.4 theory)

EXAMPLE 10



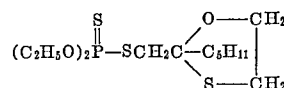
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EXAMPLE 14



2 - methyl-2-(O-methyl-O-butylphosphorodithiomethyl)-1,3-dithiocyclohexane.

EXAMPLE 15



2-amyl - 2 - (O,O-diethylphosphorodithiomethyl)-1,3-oxathiolane.

Pesticidal activity for the compounds of the foregoing examples is illustrated in Table I wherein the percentage kill is reported for a specified quantity of the candidate pesticide expressed in micrograms (hereafter termed the bio-assay test), or for a percentage concentration in aqueous dispersion (hereafter termed the screening test). A slanted line is used to separate the percentage kill, shown on the left, and the percentage concentration or quantity, shown on the right.

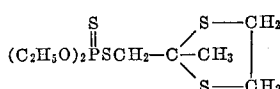
Table I

Compound (example number)	House flies, percent	American roach, percent	Milkweed bug, percent	Confused flour beetle, percent	Two-spotted mite post emb., percent	Two-spotted mite eggs, percent	Two-spotted mite systemic, p.p.m.
1.-----	100/0.1	0/0.1	0/0.1	0/0.1	100/0.1	50/0.05	100/10
2.-----	100/0.1	80/0.1	30/0.1	100/50	100/0.01	100/0.05	50/1
3.-----	92/0.1	0/0.1	-----	-----	100/0.1	75/0.1	-----
5.-----	88/0.1	20/0.1	80/0.1	0/0.1	50/0.01	50/0.01	80/10
6.-----	144/5	100/0.1	100/0.1	100/0.1	-----	-----	-----
7.-----	100/0.1	80/0.1	0/0.1	-----	50/0.005	30/0.05	96/5
10.-----	64/0.1	60/0.1	0/0.1	-----	100/0.01	50/0.01	50/1
11.-----	100/0.1	100/0.1	20/0.1	-----	90/0.005	85/0.01	98/1
12.-----	100/0.1	20/0.1	30/0.1	-----	100/0.1	75/0.05	99/1

¹ Micrograms.

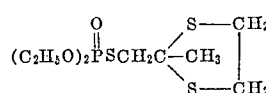
2-(O,O-dimethylphosphorodithiomethyl) - 2 - methyl-1,3-dithiolane; $N_D^{25}=1.5929$; yield=24.7 (85%); percent P=10.2 (10.7 theory); percent S=43.2 (44.2 theory).

EXAMPLE 11



2-(O,O-diethylphosphorodithiomethyl) - 2-methyl-1,3-dithiolane; $N_D^{25}=1.5632$; yield=24.5 grams (77%); percent P=9.9 (9.8 theory); percent S=38.8 (40.2 theory).

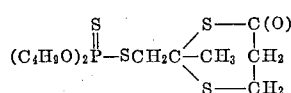
EXAMPLE 12



2-(O,O-diethylphosphorodithiomethyl) - 2 - methyl-1,3-dithiolane; $N_D^{25}=1.5371$; yield=16.0 (53%); percent P=9.8 (10.3 theory); percent S=33.2 (31.8 theory).

The following new compounds may also be prepared in reasonable yields when using the desired phosphorylated aldehyde or ketone with the corresponding glycol or mercaptan.

EXAMPLE 13



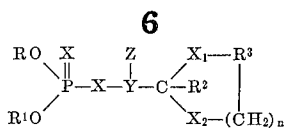
2 - methyl-2-(O,O-dibutylphosphorodithiomethyl)-1,3-dithio-4-oxo-cyclohexane.

In the screening test for the house fly, *M. domestica* (Linn.); American cockroach, *P. americana* (Linn.); spotted milkweed bug, *O. fasciatus* (Dallas); and confused flour beetle, *T. confusum* (Duval); from 10 to 25 insects were caged in cardboard mailing tubes 3 1/8 inches in diameter and 2 1/2 inches tall. The cages were supplied with cellophane bottoms and screened tops. Food and water were supplied to each cage, except in the case of the confused flour beetle which was primarily tested to determine fumigant action. Dispersions of the test compounds were prepared by dissolving 1/2 gram of the toxic material in 10 ml. of acetone. This solution was diluted with water containing 0.015% Vatsol (a sulfonate-type wetting agent) and 0.005% Methocel (methyl cellulose) as emulsifiers, the amount of water being sufficient to dilute the active ingredients to a concentration of 0.1% or below. The test insects were then sprayed with this dispersion. After 24 and 72 hours, counts were made to determine living and dead insects.

Compounds which showed high mortality in the screening test were bio-assayed on *M. domestica*. In this test, a known quantity of test compound was placed in a confined area so that it was possible to calculate the exact amount of compound per fly. The same cages were employed as for the screening test. The compound was placed in a 60 ml. petri dish along with 1 ml. of acetone containing light spray oil. After the solution air-dried, a cage containing 25 female flies was placed over the residue. Counts of living and dead insects were made after 24 and 72 hours.

The miticidal screening test for the two-spotted mite, *T. tetarius* (Linn.), involved using young pinto bean plants

1. A compound of the formula



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