

1

3,714,350
**PHOSPHORYL AND THIOPHOSPHORYL
PYRONES AS INSECTICIDES**

Stanley T. D. Gough, Raritan, N.J., assignor to
Mobil Oil Corporation

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6 Claims

ABSTRACT OF THE DISCLOSURE

New compounds from the classes of phosphoryl 2-pyrones, phosphoryl 2-pyridones and phosphoryl thio-2-pyrones are provided. The phosphorus moiety is preferably attached to the 4-position of the ring structure, and contains organic substituents attached directly to the phosphorus atom or attached thereto through an atom of oxygen or sulfur.

The new compounds are useful pesticides, and methods are provided for using them for same.

REFERENCE TO RELATED APPLICATIONS

This application is a division of copending application Ser. No. 667,380, filed Sept. 13, 1967, now abandoned.

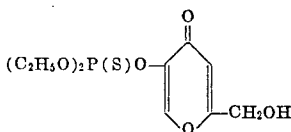
BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to new phosphorus-containing compounds and to their use as pesticides. More particularly, the invention relates to phosphoryl 2-pyrones, phosphoryl 2-pyridones and phosphoryl thio-2-pyrones and to their use in controlling pests.

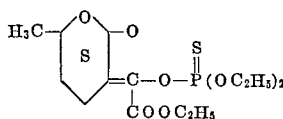
Summary of the prior art

U.S. Pat. 2,778,767 discloses phosphorus esters derived from kojic acid exemplified in particular by the diethylthiophosphate of kojic acid of the formula



U.S. Pat. 3,200,131 relates to halogenated phosphinopyranones prepared by reacting a tetrahalo α -pyrone with a trialkyl phosphite. The compounds of the reference may be illustrated by dimethoxyphosphine-trichloro-2H-2-pyranone.

Finally, German Pat. 1,198,351 discloses compounds of the type exemplified by

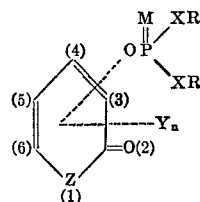


While all of the above references teach the use of the compounds disclosed therein as insecticides, neither of them, nor combinations thereof, suggest the compounds of this invention as described hereinafter.

2

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a compound of the formula



wherein the phosphorus portion is attached at one of the 3, 4, 5, and 6 positions, and wherein R and R' are from the group consisting of alkyl (C₁-C₆), cycloalkyl (C₃-C₆), alkenyl (C₂-C₆), haloalkyl (C₁-C₆), haloalkenyl, aryl and haloaryl, Y is attached at one of the 3-, 4-, 5-, and 6-positions and is from the group consisting of hydrogen, alkyl (C₁-C₆), cycloalkyl (C₃-C₆), alkenyl (C₂-C₆), haloalkyl (C₁-C₆), haloalkenyl (C₂-C₆), alkyl (α -alkylimino), aryl, alkaryl, aralkyl, haloaryl, NO₂, halogen, CN, COOR, COR, OR and SR, wherein in the last 4 members R is as already defined, X is from the group consisting of oxygen, sulfur and nothing, wherein at least one X is oxygen or sulfur, M is from the group consisting of oxygen and sulfur, n is an integer from 0 to 3, Y being the same or different when n is from 2 to 3, and Z is from the group consisting of oxygen, sulfur and NR'', wherein R'' is from the group consisting of R, R', alkaryl, aralkyl, and the members substituted with OH, CN, NH₂, OR, SR, COOR or NR₂, wherein R is already defined.

There is additionally provided a method of the control of pests, particularly insects, which comprises applying thereto a pesticidal amount of the above-defined compound.

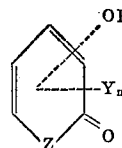
There is further provided a pesticidal composition comprising a pesticidal amount of the above-defined compound and a pesticidal carrier therefor.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In general aspect, the inventive compounds may be prepared by reaction of appropriate phosphorus compound of the formula



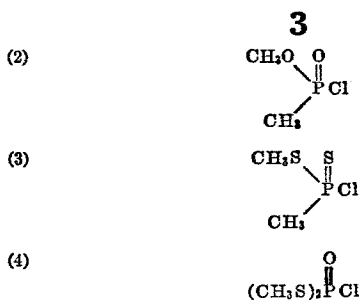
wherein R, R', X and M are as hereinbefore defined and Q is halogen, with a compound of the formula



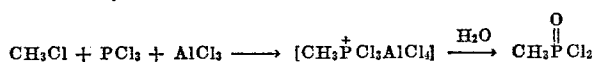
wherein Z, Y, and n are as hereinbefore defined, in the form of its salt or in the presence of acid-binding agents. Specifically, they may be prepared in accordance with the examples as set forth hereinafter.

As is apparent, the phosphorus intermediates fall into four different classes, as represented by the following specific compounds





and they may be prepared in known ways. (1) can, for example, be prepared by reacting 3 moles of methanol with 1 mole of phosphorus trichloride followed by chlorination of the resulting product. (2) can be prepared by adding 1 mole of methanol to the product obtained from the so-called Clay reaction, which reaction is represented by the following:



(3) can be synthesized by reacting methane with phosphorus trichloride at elevated temperatures in the vapor phase, reacting the product thus formed with sulfur and reacting this product with 1 mole of methyl mercaptan. (4) can be obtained by reacting 2 moles of methyl mercaptan with phosphorus oxychloride.

The starting ring compounds are known and may be prepared in known ways. Triacetic lactone, for example, is made by contacting dehydroacetic acid with 90% H_2SO_4 at 135°C . for 5 minutes. See Collie, J. Chem. Soc. 59, 609 (1891). The 3-chloro derivatives may be prepared by treating triacetic lactone with sulfuryl chloride in glacial acetic acid and recovering the crystalline material (M.P. 238°C). By bromination of triacetic lactone in acetic acid, the 3-bromo derivative is formed. See Arndt and Avan, Ber. 84, 346 (1951).

2,4-dioxo-3-ethyl (α -ethylimino)-6-methylpyrone can be obtained by the method of Garratt, J. Org. Chem. 28, 1886 (1963), i.e., reaction of dehydroacetic acid with ethylamine. The derivative having benzyl, methyl, and phenyl groups in the 3, 5, and 6 positions, respectively, is prepared by reacting propiophenone with diethyl benzylmalonate. See Goetschel and Mentzner, Bull. Soc. Chem. Fr., 365 (1962). Reaction of this derivative with aluminum chloride removes the benzyl group, and there is obtained 2,4-dioxo-5-methyl-6-phenylpyrone.

In addition, 1,6-dimethyl-4-hydroxy-2-pyridone is prepared by the method of Arndt, Eistert, Schotz and Aron (Ber. 69, 2373 (1936)), by reaction of triacetic lactone with methylamine. The 1-ethyl, 1-propyl, and 1-butyl derivatives are prepared in like manner from ethylamine, propylamine, and butylamine, respectively. The sodium salts are prepared in a manner similar to the method shown in Example 1.

The organophosphorus compounds of the present invention are stable and well-defined, and are particularly suited for pesticidal use when employed alone or in combination with carriers generally utilized in the pesticide art. The carrier adjuvants may be liquid or solid, depending upon the area to be treated, the type of pest to be controlled, and the kind of equipment available for application. When employing liquid formulations, they may be in the form of true solutions, dispersions, or emulsions.

"Solutions," as used herein, means that the compounds of the invention are of molecular size held in true solution by any suitable solvent therefor. It is noted that the inventive compounds are generally water insoluble, thus requiring an organic solvent having no phytotoxic effects when true solutions are desirable or necessary. Acetone, for example, although it will cause plant injury if kept in contact therewith, can be used as the solvent since it will dissipate rapidly when sprayed in the open, thus leaving the plant free from injury.

4

The term "dispersion" covers those liquid phases in which the active ingredient is colloidal in size and which is distributed throughout as particles held in suspension by wetting agents or by soaps. The dispersive medium is usually totally aqueous, but it may contain small quantities of organic solvent, i.e., amounts not sufficient to cause solution of the active member.

The wetting agents referred to, in addition to aiding in suspending the toxic particles, are useful as aids in uniformly distributing the active material over the area to be treated, particularly over plant areas. In other words, the wetting agent helps to prevent build-up of droplets on certain portions of the area, whereupon other portions are left untouched or insufficiently treated by the toxicant. These wetting agents are so well known to the art that it would serve no useful purpose to enumerate them here. Tween-20 (a polyethylene sorbitan monolaurate) is an example of a useful agent which can be used.

Solid formulations contemplated may be bodies of dusts or granules containing pesticidal amounts of the organophosphorus compounds of the invention. Many solids are known by the art to be useful as pesticide carriers. Examples of these are kaolin, talc, kieselguhr, diatomaceous earth, pyrophyllite, bentonite, calcium carbonate, powdered cork, wood, walnut shells and peanut shells, fuller's earth, tricalcium phosphate, and the like.

Dust or granular formulations may be prepared by grinding carrier and chemical together, followed by tumbling for a sufficient time to obtain adequate distribution of chemical. However, a more uniform product can be made if the active ingredient is dissolved in a volatile solvent, such as acetone, prior to admixing with the carrier, added to a tumbling mass of carrier, tumbled until well-mixed, and then dried in any convenient manner. The mass may be dried by applying heat thereto while tumbling or by spreading it into a thin layer and allowing it to dry in the open.

Additionally, the inventive organophosphorus compounds may be applied as aerosols, in which case it is convenient to dissolve them in any suitable solvent and to disperse this solution in dichlorofluoromethane or other chlorofluoroalkanes having a boiling point below room temperature at ambient pressures. It is contemplated that other suitable materials boiling below room temperature will also be useful for this purpose.

The concentration of the chemicals disclosed herein may vary over a wide range provided a lethal or toxic dosage thereof is placed upon the insect or in its immediate surroundings. Practically, the formulations will contain from about 0.0001 to about 1% of active ingredient by weight. Somewhat more than 1% may at times be necessary because of weather conditions, pest resistance, and the like. Usually, however, there will be no advantage in using more than 1%.

In controlling soil-borne pests, the toxicant or compositions containing it may be sprayed (if a liquid) or spread (if a solid) over the ground. Thereafter, the material may be left to the natural action of rainfall, or it may be drenched or plowed and disked into the soil. If the host is plant life, a solid formulation may be dusted onto the plant by the same method used to apply other well known solid pesticidal compositions. When liquid sprays are employed to treat plant hosts, the liquid composition may be sprayed onto the plant just to the point of liquid run-off.

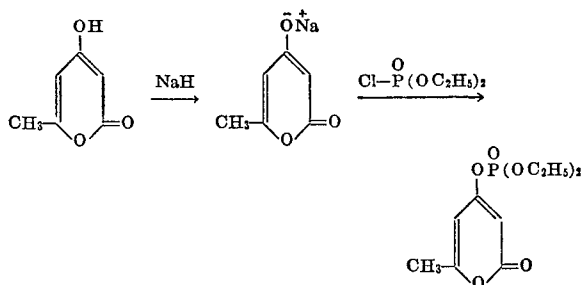
Having described the invention in general terms, the following examples of the chemicals of this invention and their use as pesticides are offered. It will be understood that the examples given merely illustrate the invention by way of specific embodiments, and thus are not to be construed as limitations upon it. The invention, with respect to the chemicals themselves and to their use against pests, is to be limited only to the extent of the broader definition set forth hereinbefore, the appended claims and reasonable equivalents flowing there-

5

from. In the examples, "parts" are parts by weight unless otherwise designated.

EXAMPLE 1

4-O,O-diethylphosphoryl-6-methyl-2-pyrone



Into a vessel equipped with a stirrer, thermometer and liquid dropping means was placed 3.0 parts of triacetic lactone (5-hydroxy-3-oxo-hex-4-enoic-acid- δ -lactone) and about 70 parts of benzene. While stirring the benzene-lactone mixture, 1.14 parts of sodium hydride as a 50% dispersion in oil was added thereto at 25° C. to effect formation of the sodium salt of the lactone. The reaction mixture was heated to reflux and maintained there for 45 minutes to insure complete reaction. Thereafter, the mass was cooled to about 25° C., and 4.1 parts of diethyl phosphorochloridate was added thereto, with stirring, over a period of 30 minutes. After refluxing for 2 hours, filtering and evaporating the solvent, 6.0 parts of 4-O,O-diethylphosphoryl-6-methyl-2-pyrone was obtained as an amber oil having the following IR and NMR analyses:

IR: C=O at 5.7 μ ; P=O at 7.7 μ ; and P—O—C at 9.6 μ .

This is consistent with the desired α -pyrone structure. NMR: A triplet at 8.65 τ , J=7 cps. (corresponding to P—O—CH₂CH₃); a quintet at 5.73 τ , J=7 cps. (corresponding to P—O—CH₂CH₃); a singlet at 7.73 τ (corresponding to C—CH₃ of ring); and two peaks at 3.8 τ and 4.07 τ (ring protons). The proton count was commensurate with the assigned structure.

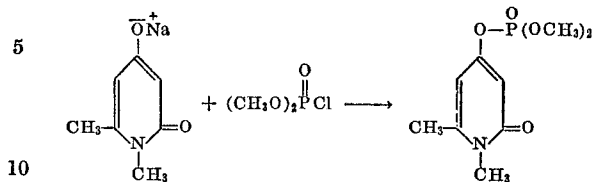
The compounds of Examples 2–23 were prepared in a manner similar to the compound of Example 1 from the sodium salt of the appropriate ring compound and the appropriate halophosphate or halophosphonate. Their NMR and IR spectra, and the integration of the NMR spectra were commensurate with the assigned structure.

Compound name	
Example:	
2.....	4-O,O-dimethylphosphoryl-6-methyl-2-pyrone.
3.....	4-O,O-dimethylthiophosphoryl-6-methyl-2-pyrone.
4.....	4-O,O-diethylthiophosphoryl-6-methyl-2-pyrone.
5.....	4-O,O-diisopropylthiophosphoryl-6-methyl-2-pyrone.
6.....	4-(S-propyl methylthiophosphonyl)-6-methyl-2-pyrone.
7.....	3-chloro-4-O,O-dimethylphosphoryl-6-methyl-2-pyrone.
8.....	3-chloro-4-O,O-dimethylthiophosphoryl-6-methyl-2-pyrone.
9.....	3-chloro-4-O,O-diethylphosphoryl-6-methyl-2-pyrone.
10.....	3-chloro-4-O,O-diethylthiophosphoryl-6-methyl-2-pyrone.
11.....	3-chloro-4-(S-propyl methylthiophosphonyl)-6-methyl-2-pyrone.
12.....	3-bromo-4-O,O-dimethylphosphoryl-6-methyl-2-pyrone.
13.....	3-bromo-4-O,O-diethylphosphoryl-6-methyl-2-pyrone.
14.....	3-ethyl(α -ethylimino)-4-O,O-diethylphosphoryl-6-methyl-2-pyrone.
15.....	3-acetyl-4-O,O-diethylphosphoryl-6-methyl-2-pyrone.
16.....	3-acetyl-4-O,O-diethylthiophosphoryl-6-methyl-2-pyrone.
17.....	3-benzyl-4-O,O-dimethylphosphoryl-5-methyl-6-phenyl-2-pyrone.
18.....	3-benzyl-4-O,O-diethylphosphoryl-5-methyl-6-phenyl-2-pyrone.
19.....	4-O,O-diethylphosphoryl-5-methyl-6-phenyl-2-pyrone.
20.....	4-O,O-diethylthiophosphoryl-6-ethyl-2-pyrone.
21.....	4-O,O-diethylphosphoryl-6-isopropyl-2-pyrone.
22.....	4-O,O-diethylthiophosphoryl-6-n-propyl-2-pyrone.
23.....	4-O,O-diethylphosphoryl-6-phenyl-2-pyrone.

6

EXAMPLE 24

1,6-dimethyl 4-O,O-dimethylphosphoryl-2-pyridone



O,O-dimethyl phosphorochloridate (4.2 parts) was added to a stirred suspension of 5.0 parts of the sodium salt of 1,6-dimethyl-4-hydroxy-2-pyridone in toluene at room temperature. The reaction mixture was stirred and refluxed overnight. After filtering the salt and evaporating the solvent to 80° C. and 15 mm., 3.2 parts of an amber oil was obtained, having the following spectra.

IR: Bands at 5.98 μ (C=O of α -pyridone), 7.7 μ (P=O), and 9.5 μ (P—O—C).

NMR: A doublet at 6.15 τ (P—O—CH₃), a singlet at 7.61 τ (C—CH₃ of ring), a singlet at 6.58 τ (N—CH₃ of ring), and a singlet at 3.9 τ (ring protons). The proton count was in agreement with the assigned structure.

The following compounds were prepared similarly to Example 24, using the appropriate chlorophosphate and the sodium salt of the appropriate pyridone. Their IR and NMR spectra, and the integration of the NMR spectra were commensurate with the assigned structures.

Compound name	
Example:	
25.....	1,6-dimethyl-4-O,O-diethylphosphoryl-2-pyridone.
26.....	1,6-dimethyl-4-O,O-diethylthiophosphoryl-2-pyridone.
27.....	1-ethyl-4-O,O-diethylphosphoryl-6-methyl-2-pyridone.
28.....	1-ethyl-4-O,O-diethylthiophosphoryl-6-methyl-2-pyridone.
29.....	1-n-propyl-4-O,O-diethylphosphoryl-6-methyl-2-pyridone.
30.....	1-n-butyl-4-O,O-diethylphosphoryl-6-methyl-2-pyridone.
31.....	1-allyl-4-O,O-diethylphosphoryl-6-methyl-2-pyridone.

EXAMPLE 32

This example will illustrate the utility of the compounds of the invention against a wide variety of household and agricultural pests.

Pest controlled and method therefor

Preparation of the formulation: A solution containing 500 p.p.m. of the compound of Example 1 was prepared by dissolving 50 mg. thereof in 5 ml. of acetone, adding 0.4 ml. of Tween-20 and diluting with 95 ml. of water. Other concentrations were prepared by diluting this with the appropriate amount of water. Solutions of other compounds were prepared similarly, unless otherwise shown.

Mexican bean beetle: Bean leaves were momentarily dipped into the test solution and were allowed to dry. After drying, a leaf was placed in a screened Petri dish and 10 beetle larvae were introduced. Results in duplicate, were taken after 24 hours.

Southern armyworm: This test is run as directed for the Mexican bean beetle, except that southern armyworm larvae were used.

Spider mite: Mite infested leaves were momentarily dipped into the test solution and were then placed (stem only) into a one-ounce bottle of water. Tests were run in duplicate, and results were recorded after 72 hours.

Housefly: Ten houseflies were placed in screened Petri dishes lined with filter paper, and the dishes were placed on a turn-table. 10 ml. of test solution was sprayed onto the dishes from a distance of one foot, using a De Vilbiss microsprayer set at 10 pounds of pressure. Tests were in duplicate, with results being taken after 24 hours.

Yellow fever mosquito larvae: A 0.2 ml. portion of the above 500 p.p.m. solution of the compound of Example 1 was diluted to 100 ml. with water to give a 1

p.p.m. solution. This was diluted with water to give other, smaller, concentrations.

In duplicate tests, ten mosquito larvae were introduced directly into the desired solution, and results were recorded after 24 hours.

German cockroach: This test was run as directed for the housefly, except that the German cockroach was substituted therefor.

Bean aphid: Fifty mg. of the compound of Example 1 was dissolved in 100 ml. of acetone containing 10 drops of Tween-20 to give a concentration of 500 p.p.m. This was diluted with more acetone to give other concentrations.

Nasturtium leaves infested with bean aphids were placed in screened Petri dishes lined with filter paper. 10 ml. of the test solution was sprayed onto the dishes from a distance of 1 foot, using a De Vilbiss microsprayer set at 15 pounds of pressure. Spraying was done in a spray hood, with the dishes resting on a turntable rotating at 30 r.p.m. Tests were in duplicate, with results being taken after 24 hours.

Boll weevil: The test solution (500 p.p.m.) was prepared as shown for the bean aphid test. Other concentrations were prepared by dilution with acetone.

Ten boll weevil larvae were placed in a screened Petri dish lined with filter paper, and the dishes were placed on a turntable in a spray hood. 20 ml. of the test solution was sprayed onto the dishes from a distance of 1 foot, using a De Vilbiss microsprayer set at 15 pounds of pressure, while the turntable was rotating at 30 r.p.m. Tests were run in duplicate, and results were taken after 48 hours.

RESULTS.—COMPOUND OF EXAMPLE 1

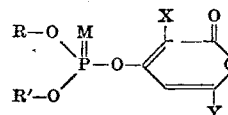
Pest.....	Percent control				
	500 p.p.m.	100 p.p.m.	10 p.p.m.	1 p.p.m.	0.1 p.p.m.
Mexican bean beetle.....	50	-----	-----	-----	-----
Southern armyworm.....	70	-----	-----	-----	-----
Spider mite.....	100	90	70	-----	-----
Housefly.....	100	50	-----	-----	-----
Mosquito larvae.....	-----	-----	-----	100	45
German cockroach.....	90	50	20	-----	-----
Bean aphid.....	100	100	90	-----	-----
Boll weevil.....	100	90	30	-----	-----

The following compounds were tested as outlined above, using test solutions containing 500 p.p.m., except that 1 p.p.m. was used for the Mosquito Larvae (ML) test.

Compound.....	MB	SA	SM	HF	ML	GC	BA	BW
Example:								
2.....	100	90	100	100	90	20	100	90
3.....	-----	60	100	90	100	-----	90	90
4.....	-----	80	100	50	100	-----	100	100
5.....	20	50	100	20	-----	-----	90	70
6.....	-----	30	80	-----	-----	-----	-----	-----
7.....	-----	-----	70	-----	-----	-----	70	20
8.....	-----	-----	-----	-----	-----	-----	30	20
9.....	-----	-----	100	100	70	30	100	30
11.....	-----	-----	50	-----	-----	-----	20	-----
12.....	40	-----	70	20	-----	-----	40	-----
13.....	-----	-----	100	-----	-----	-----	30	30
14.....	20	-----	70	-----	-----	-----	20	20
15.....	100	-----	-----	40	-----	-----	100	60
16.....	-----	-----	40	50	-----	-----	70	50
17.....	-----	-----	20	20	-----	-----	20	20
18.....	-----	-----	-----	20	-----	-----	20	-----
19.....	-----	-----	60	20	20	-----	80	60
24.....	100	100	100	100	100	30	100	100
25.....	40	80	100	90	100	-----	100	100
26.....	100	80	90	30	100	-----	70	60
28.....	100	70	90	70	100	-----	100	100

I claim:

1. A method for controlling insects which comprises applying thereto an insecticidal amount of a compound of the formula:



wherein R and R' are alkyl of 1-4 carbon atoms, M is oxygen or sulfur, X is hydrogen or halogen, and Y is alkyl of 1-6 carbon atoms.

2. The method of claim 1 in which the compound is 4-O,O-dimethylthiophosphoryl-6-methyl-2-pyrone.

3. The method of claim 1 in which the compound is 3-chloro-4-diethylphosphoryl-6-methyl-2-pyrone.

4. The method of claim 1 in which the compound is 4-O,O-diethylphosphoryl-6-methyl-2-pyrone.

5. The method of claim 1 in which the compound is 4-O,O-dimethylphosphoryl-6-methyl-2-pyrone.

6. The method of claim 1 in which the compound is 4-O,O-diethylthiophosphoryl-6-methyl-2-pyrone.

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ALAN L. ROTMAN, Primary Examiner

U.S. Cl. X.R.

260—294.8 K, 294.9, 295 R, 296 R, 297 P