Patented Jan. 10, 1950

2,494,284

UNITED STATES PATENT OFFICE

2,494,284

CYANOALKYL PHOSPHATES AND METHOD OF PREPARATION

Jack T. Cassaday and Erick I. Hoegberg, Stamford, and Bruce D. Gleissner, Riverside, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

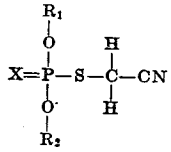
No Drawing. Application January 12, 1949, Serial No. 70,604

13 Claims. (Cl. 260—461)

1

The present invention relates to new and useful organic phosphate compounds and the method of preparation thereof.

These new compounds are phosphate esters which conform to the general formula

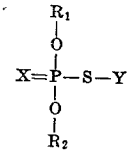


in which R_1 and R_2 are chosen from the group consisting of alkyl and aryl hydrocarbon radicals and X is a member of the group consisting of sulfur and oxygen.

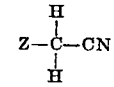
In the new compounds R_1 or R_2 may be the same or different radicals. Furthermore, it is to be understood that when R_1 and R_2 stand for alkyl radicals, they represent both the straight chain and branch chain, the saturated and unsaturated, and the cycloaliphatic hydrocarbon radicals. Typical examples of these radicals are methyl, ethyl, n-propyl, isopropyl, isobutyl, sec.-amyl, n-hexyl, 2-ethylhexyl, n-octyl, n-decyl, n-dodecyl, oleyl, cetyl, ceryl, allyl, cyclohexyl, phenyl and naphthyl.

The compounds of this invention possess general pest-control characteristics, including insecticidal, rodenticidal, and fungicidal properties. They may also be employed as corrosion inhibitors, plasticizers, flotation agents, and petroleum additives.

The phosphate esters of the above general formula may be readily prepared by reacting a phosphate of the formula



in which R_1, R_2 and X have the meaning shown above, and Y represents an alkali-forming metal, with a halogen-substituted acetonitrile of the formula

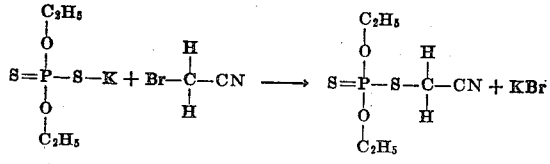


in which Z is a member of the group consisting of chlorine and bromine.

The term "alkali-forming metal" as used in this specification and in the appended claims is intended to cover the alkali metals (including ammonium), and the alkaline earth metals.

2

A typical reaction in which potassium O,O-diethyl dithiophosphate is reacted with monobromoacetonitrile to produce S-cyanomethyl O,O-diethyl dithiophosphate may be illustrated as follows:



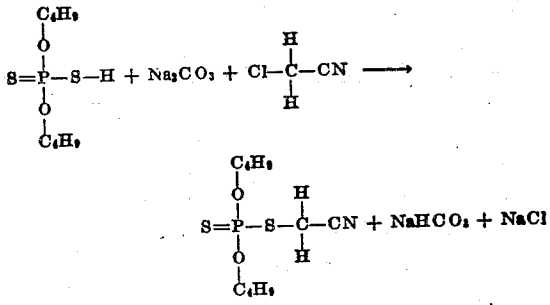
High yields of the desired products are obtained by carrying out the reaction in the presence of a solvent. Such solvents include the low molecular weight aliphatic monohydric alcohols, the ketones such as, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl benzyl ketone, cyclohexanone, acetophenone, and the like; aliphatic esters such as ethyl acetate, amyl acetate, 2-ethylhexyl acetate, methyl proprionate, methyl butyrate, ethyl butyrate and isopropyl butyrate; dioxane, nitrobenzene, chlorobenzene, toluene, xylene, chloroform, carbon tetrachloride, 1,2-dimethoxyethane and the trialkyl phosphates such as trimethyl phosphate, triethyl phosphate and triisopropyl phosphate.

The reaction is preferably carried out at a temperature within the range of from about 20° C. to 150° C. However, temperatures outside of this range may be employed depending upon the type of reactants and solvents utilized.

An alternative method of preparing the above compounds consists in employing in lieu of the alkali-forming metal phosphate the corresponding acid and a basic alkali-forming metal compound, the latter having sufficient alkalinity to neutralize said acid. Obviously, this procedure avoids the initial preparation and isolation of the alkali-forming metal phosphate. Such basic alkali-forming metal compounds include sodium carbonate, potassium carbonate, barium carbonate, magnesium carbonate, lithium carbonate, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide, magnesium hydroxide, sodium hydrosulfide, sodium borate, tripotassium arsenate, tripotassium arsenite, sodium pyrophosphate, magnesium pyrophosphate, potassium pyrophosphate, barium phosphate, trisodium phosphate, and the like.

Employing the above procedure in the preparation of S-cyanomethyl O,O-di-n-butyl dithio-

phosphate, the reaction may be illustrated as follows:



The following examples in which the parts are by weight further illustrate the invention.

Example 1

19.6 parts of potassium O,O-dimethyl dithiophosphate, 7.6 parts of monochloroacetonitrile and 150 parts of acetone were mixed together and allowed to stand at room temperature (20°–25° C.) for 6 days. The precipitated potassium chloride was filtered off and the filtrate was heated under vacuum to remove the acetone. The residual liquid was washed with cold water and dried over anhydrous sodium sulfate, giving 9.3 parts of S-cyanomethyl O,O-dimethyl dithiophosphate, a colorless oily liquid, having a refractive index N_D^{25} 1.5306.

Example 2

The procedure of Example 1 was employed, using 20.8 parts of sodium O,O-diethyl dithiophosphate, 12 parts of monobromoacetonitrile and 100 parts of acetone. The mixture was allowed to stand at room temperature for 2 days. The product, S-cyanomethyl O,O-diethyl dithiophosphate, was an amber-colored liquid, having a refractive index N_D^{25} 1.5153.

Example 3

The procedure of Example 1 was employed, using 8.9 parts of potassium O,O-diphenyl dithiophosphate, 2.27 parts of monochloroacetonitrile and 100 parts of acetone. The mixture was allowed to stand at room temperature for 2 days. The product, S-cyanomethyl O,O-diphenyl dithiophosphate, was an amber-colored oily liquid having a refractive index N_D^{25} 1.5180.

Example 4

The procedure of Example 1 was employed, using 15.4 parts of potassium O,O-di-n-amyl dithiophosphate, 3.8 parts of monochloroacetonitrile and 100 parts of acetone. The product, S-cyanomethyl O,O-di-n-amyl dithiophosphate, was a straw-colored liquid having a refractive index N_D^{25} 1.4984.

Example 5

The procedure of Example 1 was employed, using 20.8 parts of potassium O,O-diethyl monothiophosphate, 12 parts of monobromoacetonitrile and 75 parts of methyl isobutyl ketone. The mixture was held at 60° C. for 5 hours and then cooled and filtered to remove the precipitated potassium bromide. 12 parts of S-cyanomethyl O,O-diethyl monothiophosphate were obtained as a brown oily liquid.

Example 6

40 parts of O,O-diethyl dithiophosphoric acid (93%) were added slowly to a well-agitated mixture of 21.2 parts of anhydrous sodium carbonate suspended in 100 parts of ethanol. 15.1 parts of monochloroacetonitrile were then added slowly and the mixture was heated under reflux with stirring for a period of 6½ hours. The reaction mixture was filtered and the filtrate was heated under vacuum to distill off the ethanol. The residual oily liquid was washed with cold water and dried over anhydrous sodium sulfate. 37 parts of the product, S-cyanomethyl O,O-diethyl dithiophosphate, were obtained.

Example 7

The procedure of Example 6 was employed, using 41 parts of O,O-di-n-decyl dithiophosphoric acid, 7.9 parts of sodium hydrosulfide (71%), 200 parts of acetone and 12 parts of monobromoacetonitrile. The mixture was not heated under reflux as in Example 6, but was allowed to stand for 2 days at room temperature. The product, S-cyanomethyl O,O-di-n-decyl dithiophosphate, was obtained in a 93% yield as a red oily liquid.

The phosphate esters of this invention may be employed in controlling many types of insects and mites such as, for example, the black bean aphid, green peach aphid, pea aphid, chrysanthemum aphid, greenhouse thrips, California red scale, citrus red spider, greenhouse red spider, milkweed bug, mealy bug, sow bug, German cockroach, Southern army worm, yellow fever mosquito, malarial mosquito, Mexican bean beetle, confused flour beetle, and black carpet beetle.

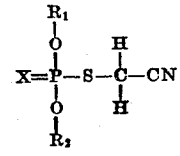
These new compounds may also be used in combination with insecticides such as lead arsenate, nicotine, rotenone, pyrethrum, benzene hexachloride, 1,1,1 - trichloro - 2,2 - di(p - chlorophenyl) ethane, dodecyl thiocyanate, phenothiazine, and the like; with fungicides such as sulfur, various copper compounds, mercury salts, and the like; and with various types of plant foods and fertilizers.

This application is a continuation-in-part of our copending application Serial Number 6348, filed February 4, 1948.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto, but is to be construed broadly and restricted solely by the scope of the appended claims.

We claim:

1. Phosphate esters of the general formula



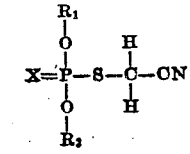
in which R_1 and R_2 are chosen from the group consisting of alkyl and aryl hydrocarbon radicals, and X is a member of the group consisting of sulfur and oxygen.

2. S-cyanomethyl O,O-diethyl dithiophosphate.

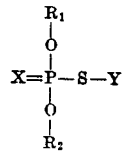
3. S-cyanomethyl O,O-diphenyl dithiophosphate.

4. S-cyanomethyl O,O-diethyl monothiophosphate.

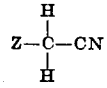
5. A method of preparing a phosphate ester of the general formula



in which R_1 and R_2 are chosen from the group consisting of alkyl and aryl hydrocarbon radicals, and X is a member of the group consisting of sulfur and oxygen, which includes the step of reacting a phosphate of the general formula



in which R_1 and R_2 are chosen from the group consisting of alkyl and aryl hydrocarbon radicals, and X is a member of the group consisting of sulfur and oxygen, and Y represents an alkali-forming metal, with a halogen-substituted acetonitrile of the formula

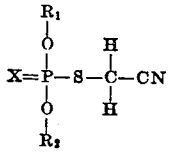


in which Z is a member of the group consisting of chlorine and bromine.

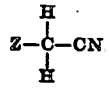
6. The method of claim 5 in which the reaction is carried out in the presence of a solvent.

7. The method of claim 5 in which the reaction is carried out at a temperature within the range of from about 20° C. to 150° C.

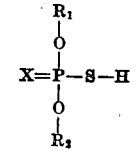
8. A method of preparing a phosphate ester of the general formula



in which R_1 and R_2 are chosen from the group consisting of alkyl and aryl hydrocarbon radicals, and X is a member of the group consisting of sulfur and oxygen, which includes the step of reacting together a halogen-substituted acetonitrile of the formula



in which Z is a member of the group consisting of chlorine and bromine, an acid phosphate of the general formula



in which R_1 and R_2 are chosen from the group consisting of alkyl and aryl hydrocarbon radicals, and X is a member of the group consisting of sulfur and oxygen, and a basic alkali-forming metal compound having sufficient alkalinity to neutralize the acid phosphate.

9. The method of claim 8 in which the basic alkali-forming metal compound is sodium carbonate.

10. The method of claim 8 in which the reaction is carried out in the presence of a solvent.

11. A method of preparing S-cyanomethyl O,O-diethyl dithiophosphate which includes the step of reacting together O,O-diethyl dithiophosphoric acid, sodium carbonate and monochloroacetonitrile in the presence of ethyl alcohol.

12. A method of preparing S-cyanomethyl O,O-diphenyl dithiophosphate which includes the step of reacting together potassium O,O-diphenyl dithiophosphate and monochloroacetonitrile in the presence of acetone.

13. A method of preparing S-cyanomethyl O,O-diethyl monothiophosphate which includes the step of reacting together potassium O,O-diethyl monothiophosphate and monobromoacetonitrile in the presence of methyl isobutyl ketone.

JACK T. CASSADAY.
ERICK I. HOEGBERG.
BRUCE D. GLEISSNER.

No references cited.