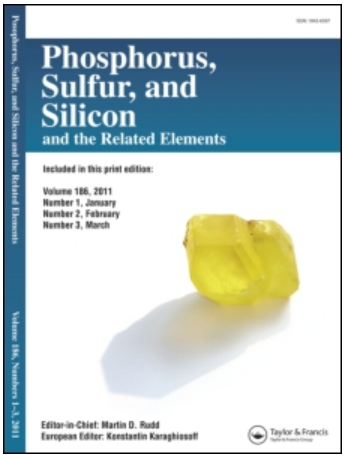

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Organophosphorus Growth Regulators and Inductors of Plant Resistance

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To cite this Article Zavlin, P. M. , Matevosyan, G. L. and Ofengeim, D. L.(1999) 'Organophosphorus Growth Regulators and Inductors of Plant Resistance', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 629 — 632
To link to this Article: DOI: 10.1080/10426509908546323
URL: http://dx.doi.org/10.1080/10426509908546323

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 629-632
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Organophosphorus Growth Regulators and Inductors of Plant Resistance

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Based on investigations of physiological mechanisms of phytohormonal action, the purposeful synthesis of new growth regulators and inductors of plant resistance in the range of phosphorylated nitrogen heterocycles imidazoles, benzimidazoles, purines, and chitozan has been performed.

Keywords: phosphorylated nitrogen heterocycles; growth regulators of plant

INTRODUCTION

Our work devoted to the problem of the purpose-oriented synthesis of new growth regulators and inductors of plant resistance based on various studies of physiological mechanisms of phytohormon action. The synthesis was performed in the range of phosphorylated nitrogen heterocycles-imidazoles, benzimidazoles, benztriazoles, purine,and chitosan.

Results:

In the interaction of imidazoles, benzimidazoles, and benztriazoles with chloranhydrides of phosphorous acids in tetrahydrofurans in the presence of triethylamine, with great yield, mono-,di-, and tri-(1-imidazolyl)-,(1-benzimidazolyl), and (1-benztriazolyl)- phosphite

phosphate, and thiophosphate have been prepared.

For the study of the dependence between biological activity of phosphorylated azoles and their structures, the N-Phosphonalkylated azoles have been synthesized. The synthesis of N-phosphonmethylated azoles was based on the Kabachnik and Fields reaction. Electron-donating substitutes in azoles hasten the reaction of phosphonmethylation, but electron-withdrawing groups hinder the reaction. N-phosphonmethylated azoles can also be prepared by the reaction of azoles with diethylphosphite and aminals. N-phosphonaminoazoles can be formed from azoles, p-nitrosodimethylaniline, and diethylphosphite.

For the preparation of N-phosphonethyl derivatives of azoles, the reaction of azoles and di(β-chlorethoxy) vinylphosphonate has been studied. The most efficient way of producing very active phytoregulator, "Diphoset", is the reaction of 2-benzylbenzimidazole with di(β-chlorethoxy) vinylphosphonate in conditions of phase transfer catalysis. In the absence of a catalyst in the reaction between azoles and di(β-chlorethoxy) vinylphosphonate , nucleophilic substitution at the β-carbon atom of the β-chlorethoxy groups of di (β-chlorethoxy) vinylphosphonate takes place.Phosphorylated azoles with double bonds can accept both nucleophile and electrophile.

N-phosphonpropylbenzimidazole produced from N-allylbenzimidazole and diethylphosphite in the presence of tertiary butyl hydroperoxide . N-phosphonpropylbenzimidazole can also be prepared by adding bromine to N-allylbenzimidazole and then 1-N-(3'-diethylphosphon-2'-brompropyl) benzimidazole can easily be prepared by the Arbusov Reaction. The final product was made from the latter, by reduction. Dialkylphosphite added to N-allylbenzimidazole, likewise, gives N-phosphorylpropylbenzimidazole, when the reaction is catalyzed with a base. Benzimidazole added to allylphosphonate produces the same N-phosphorylpropylbenzimidazole in a reaction catalyzed by an acid. Organophosphorous growth regulators of prolonged action have been prepared by homo- and hetero- polycondensation of di(β-chlorethoxy) β-(1-azolyl) ethylphosphonates. Growth regulators of prolonged action can also obtained by the reaction of N-glicidylphosphorylbenzimidazole with gelatin.

2-phosphorelated-1,3-diazoles were produced directly by treatment of N-acetyl-1,3-diazoles, like, N-acetylbenzimidazole with chloranhydrides of phosphorous acids.

As known, the phytoregulators in the range of ethanolamine characterized by antistress action. On the other hand, its very important

to synthesize phosphorylated benzimidazole analog of ADP. For this reason the interaction 2-hydroxymethylbenzimidazole with chloranhydrides of phosphorous acid has been carefully researched. As was shown, N-phosphorylated compounds prepared by treatment of 2-hydroxybenzimidazoles with chloranhydrides of phosphorous acids in the presence of a base. In the absence of a base O-phosphorylated derivatives of 2-hydroxybenzimidazoles are formed. Good yields of 5-phosphorelated benzimidazoles can be obtained, when 5,6-dinitrobenzimidazole are treated with dialkylphosphite. For the comparison cytokinine activity of phosphorylated benzimidazoles with purines, 6-phosphorylated purines have been obtained.

In order to study the metabolism and the mechanism of phytoregulating action of phosphorylated azoles and their behavior in a biological media we have synthesized their ^{32}P labeled derivatives. These derivatives were prepared by radiation of solutions of benzimidazole in tetrachlormethane, in Po-Be reactor.In order to obtain ^{32}P labeled phosphonethylbenzimidazoles, we have successfully synthesized a phosphonatic reagent-di(β-chlorethoxy) vinyl^{32}P labeled phosphonate. Using the methods of gas-liquid and ^{32}P labeled radiochromatagraphy we looked closely at the behavior of phosphorylated benzimidazoles in water, soil, and plants. We have found that phosphorylated benzimdazoles have the ability to stimulate plant growth and quicken the degradation of phosphororganic and piretroidal insecticides, when being applied in a combination.

In our work new growth regulators and inductors of plant resistance in the range of phosphorylated chitosan have also been studied. Phosphonmethylated chitosan can be prepared by Kabachnik-Fields reaction. It was found that the direction of this reaction and structure of the products of phosphorylation of chitosan depend on the nature of phosphorylating agent, reagents ratio and the conditions of interaction. The reaction of chitosan with diethylphosphite proceeds both alongside the scheme on the slide of esterification of hydroxyl groups (I) and phosphonmethylation of amino groups with formaldehyde(II). The conditions were found for obtaining co-polymers containing chitosan phosphites and chitosan with phosphonmethylated amino groups.

Biological activity of these synthesized compounds, as growth regulators and resistant inductors of plants, was studied by the four step screening. During each step of the screening, complex of biological studies were done, aimed at determining the spectrum of their physiological action, of their optimum growth regulation concentration,

and their compatibility with pesticides. The biological object of the study were cereal and vegetable plants. The influence of synthesized compounds-phosphorylated nitrogen heterocycles-imidazoles,benzimidazoles, purines,and chitozan on the phytohormonal balance of plants has been researched. The cytokinine activity of phosphorylated benzimidazoles has been revealed.

The results of the studies of new phytoregulators showed the increase in plant resistance to unfavorable stress action, illnesses, phytotoxic herbicides and simultaneously increased the height growth stimulation. Among these synthesized compounds we have found very effective inductors of resistance to low temperatures, to black stem, and to root diseases of cabbage. These compounds also increase the resistance to porodery mildew and to antracknose disease of cucumber, and to tomato mosaic virus. The increased resistance of the tomato plant to the mosaic virus occurs because of the stimulation of pigment biosynthesis, especially choraphyl *a*, which results in an increase of photosythesis. The complex application of growth regulators like, "Diphoset", for the treatment of seeds and sprouts, "gibbersib" for gibberellric stimulation, and "entox", gamair", and "aphydol", for the treatment of flower in a combination with biofungicides, increase a plants stability to wreckers, illnesses and promote the increase tomato productivity in hot houses by 35-45%. The complex application of phosphorylated azoles like " Diphoset", "Tribiphos", and phosphorylated chitosan, with fungicides, herbicides, and insecticides, with cultivation of beets, carots, and cabbage showed that these compounds stimulated the growth and the development of plants, raised stability to adverse conditions, illnesses, and increased productivity by 20-60%. It is determined that the use of the new phytoregulators increases cellular membrane penetration in relation to plasmolem and tonoplast. The result is the increase of cell stability to the influence of the cell's exterior. The adaptational activities of phosphorylated benzimidazoles is stimulated by the biological synthesis of endogenic phytohormones, especially cytokinine. In increasing barrier activities of the cellular membranes the adaptational activities of phosphorylated benzimidazoles is also increased. We have concluded that phosphorylated benzimidazoles, not only have the ability to stimulate plant growth, but also to quicken the degradation of phosphororganic and piretroidal insecticides, when being applied in a combination. Using the methods of gas-liquid and ^{32} P labeled radiochromatagraphy, we have studied the behavior of phosphorylated benzimidazoles in water, soil, and plants.

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 633-636
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Synthesis and Dealkylation of 1-(Dichloro-Phenoxyacetoxy)Alkyl Phosphonates

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Using the silylation procedure with chlorotrimethylsilane/sodium iodide followed by alcoholysis, 1-(dichlorophenoxy acetoxy)alkyl phosphonic acid dimethyl esters can be transformed into the parent phosphonic acids without influence on carboxylate ester group.

Keywords: condensation; dealkylation of phosphonates; trimethylsilyl chloride/sodium iodide; phosphonic acid

INTRODUCTION

In the course of our research for new phosphonate derivatives with good biological activities, a series of oxophosphonic acid derivatives have been investigated in recent years[1]. Some substituted phenoxy acetoxy alkyl phosphonates have shown herbicidal activities, its corresponding phosphonic acids would be of better biological interest. Therefore, we are interested in extending our investigations to alkyl phosphonic acid with substituted phenoxy acetoxy group such as dichlorophenoxy acetoxy group and finding a mild and efficient method for conversion of dimethyl phosphonate to the corresponding acid.

RESULTS AND DISCUSSIONS

1-(Dichlorophenoxy acetoxy) Alkyl Phosphonic Acid Dimethyl Ester

The following synthetic route A and B can be used to obtain the title compounds 8a-g, respectively.