Translated from *Uspekhi Khimii* **61** 1839–1863 (1992) U.D.C. 547.341

Phosphorus derivatives of salicylic acid

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ABSTRACT. The present state of work on the methods of synthesis, chemical properties, and practical applications of phosphorus-containing derivatives of salicylic acid has been reviewed. The characteristics of the chemical transformations of cyclic and acyclic phosphorus derivatives of salicylic acid related to the coordination state of the phosphorus atom have been examined.

The bibliography contains 158 references.

Contents

I. Introduction 1009
II. Cyclic phosphorus-containing derivatives of salicylic acid 1009
III. Acyclic phosphorus-containing derivatives of salicylic acid 1016

I. Introduction

Acyl derivatives of salicylic acid are used as drugs and microbiocides. Particular mention may be made of the use of acetylsalicylic acid as an analgesic and antipyretic.[1] Many organophosphorus compounds show a wide spectrum of biological activity.[2] The study of compounds whose molecules contain fragments of phosphorus acids and salicylic acid is of considerable interest in the search for new substances of practical importance. Although phosphorus derivatives of salicylic acid have been the subject of a large number of studies, no reviews have been published, except for selections from the literature devoted to individual aspects of the chemistry of these compounds.[3–7] Monographs on the chemistry of phosphorus compounds contain few data on phosphorus derivatives of salicylic acid.

In our opinion, phosphorus derivatives of salicylic acid deserve detailed examination not only because of their low and varied biological activity but also because of their unique reactivity, which differs sharply from that of usual acyl derivatives of phosphorus.

The aim of the present review is to summarise and where possible systematise the results of work on the methods of synthesis and reactivity of phosphorus derivatives of salicylic acid.

Salicylic acid, unlike other hydroxybenzoic acids, contains in the *ortho*-position two functional groups capable of reacting with a central phosphorus atom to give cyclic and acyclic phosphorus-containing derivatives. The chemical properties of phosphorus derivatives of salicylic acid are determined to a large extent by their cyclic or acyclic structure, and also depend on the coordination state of the phosphorus atom. These characteristics were taken as a basis for the systematisation in the compilation of the present review.

II. Cyclic phosphorus-containing derivatives of salicylic acid

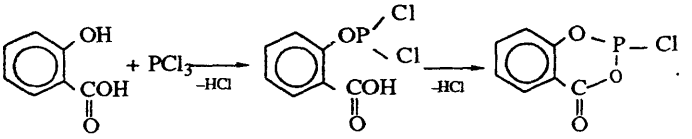
1. Cyclic phosphorus derivatives of salicylic acid containing a three-coordinate phosphorus atom

The phosphorus derivatives of salicylic acid are mixed anhydrides of phosphorus and salicylic acids. Certain features of the chemistry of these compounds are similar to those of the chemistry of acyl phosphites with an endocyclic fragment, described earlier.[8]

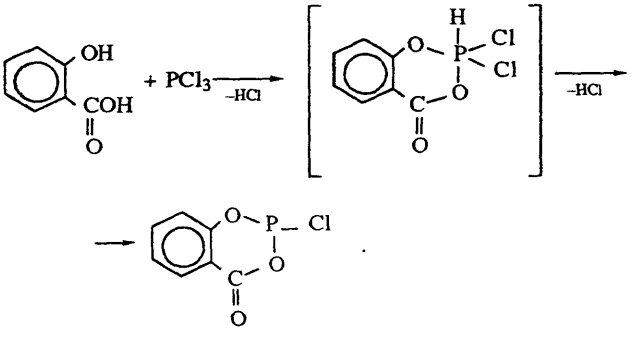
a. 4,5-Benzo-2,6-dioxaphosphorin-3-ones (BDPO)

Phosphorus derivatives of salicylic acid were first obtained by Anschütz and co-workers[9] by the reaction of salicylic acid with phosphorus trichloride. This reaction can give several products, whose structures have been studied by a number of authors.[5,6,9–16] The results of these studies have been summarised by Atherton.[4] It was established that when stoichiometric quantities of the starting materials or an excess of phosphorus trichloride are used, the chief product is 1-chloro-4,5-benzo-2,6-dioxaphosphorin-3-one (1-Cl-BDPO)—a cyclic salicyl chlorophosphite with a three-coordinate phosphorus atom in the ring. Despite the extensive practical application of phosphorylation by P^{III} chlorides in the preparation of salicyl phosphites, the mechanism of this reaction has not been studied in detail.

It has been suggested that the mechanism involves phosphorylation of the phenolic hydroxyl group, followed by ring closure:[14,15]



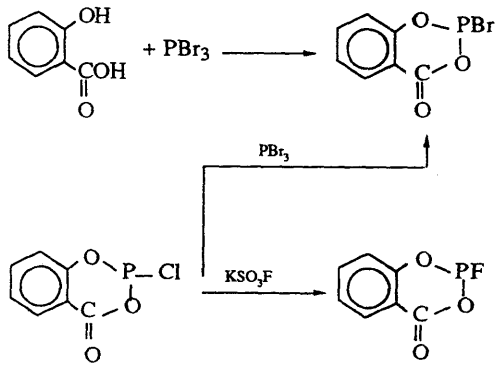
A number of authors suggest that the reaction takes place via a stage involving the formation of a phosphorane.[10,16] No spectroscopic confirmation of intermediate structures of this kind has been obtained, however.



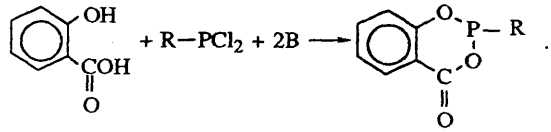
The reaction of salicylic acid with phosphorus trichloride is usually carried out by heating their mixtures in benzene, toluene, or xylene for 2–4 h,[12,14,17] or in ether with a hydrogen chloride acceptor,[15] and the product is isolated by vacuum distillation. Cooling gives a crystalline product with m.p. 36–37 °C. The ^{31}P NMR spectrum of 1-Cl-BDPO contains one signal due to the phosphorus nucleus, at 151 p.p.m.[18]

Derivatives of salicylic acid containing chlorine, bromine, iodine, methyl and nitro-groups,[11] and the hydroxyl group[19] in the benzene ring also react with phosphorus trichloride. The cyclic products were obtained in 69–90% yield.

The reaction of salicylic acid with phosphorus tribromide gives a high yield of 1-bromo-4,5-benzo-2,6-dioxaphosphorin-3-one,[14] which has also been obtained by replacing chlorine by bromine.[20] 1-F-BDPO has been synthesised by an exchange reaction.[21]



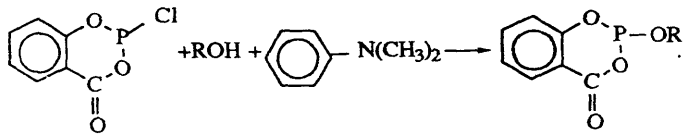
Salicylic acid undergoes a cyclisation with the dichlorides of phosphorus(III) acids in the presence of a hydrogen chloride acceptor:[15,22–24]



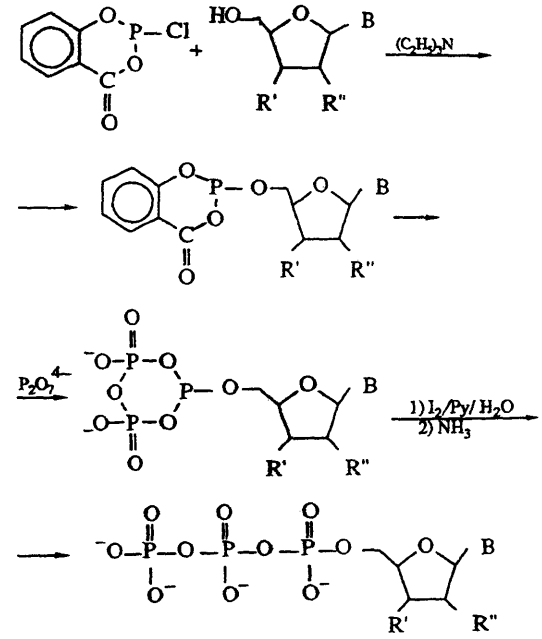
The 1-phenyl-4,5-benzo-2,6-dioxoaphosphorin-3-one formed in this reaction has been used to obtain copolymers with *ortho*- and *para*-substituted aldehydes, 4,4′-diphenoquinones, methacrylate, and acrolein.[25–27]

1-Chloro-4,5-benzo-2,6-dioxaphosphorin-3-ones react readily with electrophilic and nucleophilic reagents. These reactions can take place both with preservation and with splitting of the dioxaphosphorine ring, and with preservation or change in the coordination of the phosphorus atom. The chemical properties of these compounds have been most fully studied for 1-Cl-BDPO. As shown by Nesterov and co-workers,[28–32] this compound can serve as a key intermediate in the synthesis of various types of phosphorus derivative of salicylic acid.

The chlorine atom in position 1 of the phosphine ring has practically the same mobility as that in alkylene chlorophosphites. Thus the reaction of 1-Cl-BDPO with alcohols and phenols in the presences of a hydrogen chloride acceptor gives 1-alkoxy(aryloxy)-4,5-benzo-2,6-dioxaphosphorin-3-ones.[14,22,28–31,33,34]

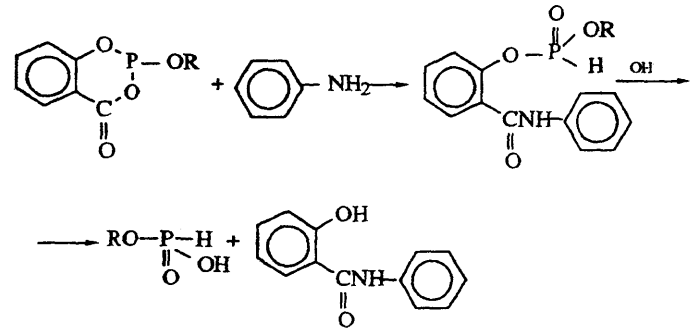


1-Alkoxy(aryloxy)-BDPO are also highly reactive, and react readily with nucleophilic reagents, with splitting of the dioxaphosphorine ring. When an excess of the alcohol or phenol is used, the chief products are salicylic acid and trialkyl(aryl) phosphites.[28,35] Carrying out this reaction in stages provided the basis for an extremely effective method for synthesising nucleoside polyphosphates.[36–39]

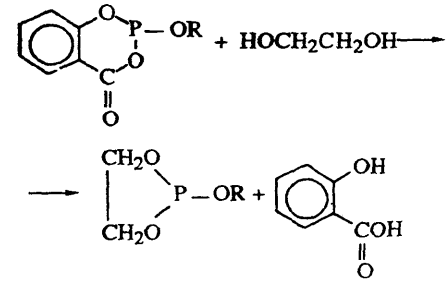


B represents nucleic bases (A^{Bz}, G^{ib}, T, C^{Bz}, U).

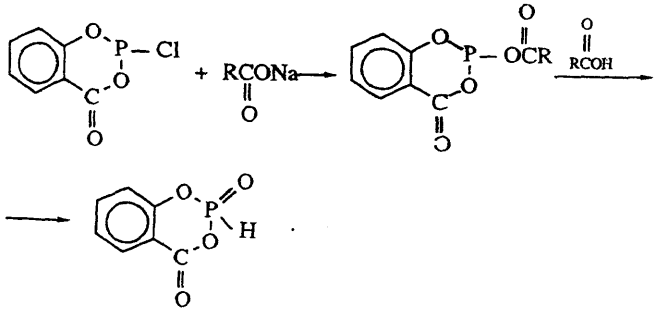
The reactions of 1-alkoxy-BDPO with amines gives monoalkyl phosphites.[40]



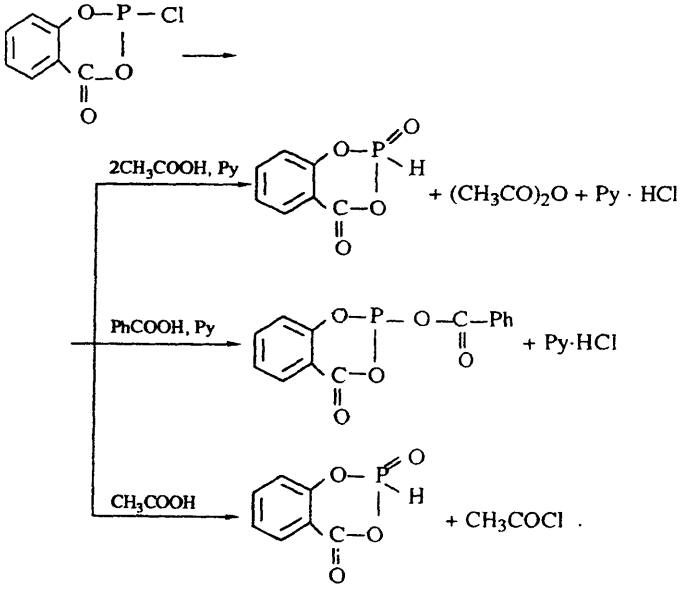
1-Alkoxy-BDPO undergo exchange reactions. With glycols, an extremely interesting reaction takes place, with recyclisation of the phosphorine ring to give a phospholane ring.[41]



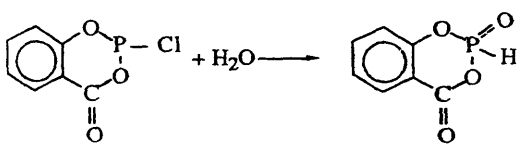
The high mobility of the chlorine atom in 1-Cl-BDPO is confirmed by the reaction with such weak nucleophilic reagents as the salts of carboxylic acids, accompanied by the replacement of the chlorine atom by the acyloxy-group[14,35] and the formation of a mixed anhydride of salicyclic, phosphorus, and carboxylic acids. With an excess of acid, the anhydride undergoes splitting, accompanied by the formation of a cyclic hydrophosphoryl compound[14,35] — 1-hydro-4,5-benzo-2,6-dioxaphosphorine-1,3-dione (1-H-BDPD):



The reaction of salicylic chlorophosphite with carboxylic acids have been studied.[14,22,35] The reaction with benzoic acid gave the acyl phosphite, but the reaction with acetic acid gave salicyl hydrogen phosphite, despite the presence of a base.

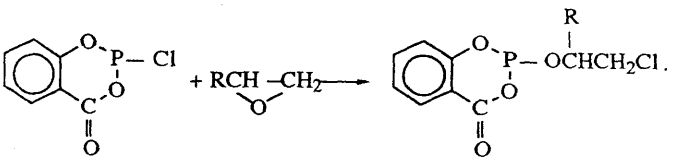


The last reaction is the most convenient preparative method for obtaining 1-H-BDPD. 1-H-BDPD can also be obtained by the reaction of 1-Cl-BDPO with water:[15,42]

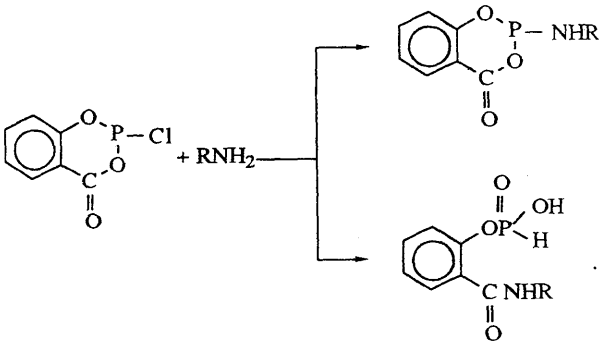


Like other hydrophosphoryl compounds, 1-H-BDPD exists in two tautomeric forms, with three-coordinate and four-coordinate phosphorus atoms, and the ^{31}P NMR spectrum correspondingly contains signals due to phosphorus nuclei at 113 p.p.m. and −4 p.p.m.[43] According to recent data,[44] however, a close structural analogue — pyrocatechol hydrogen phosphite — exists only in the oxo-form.

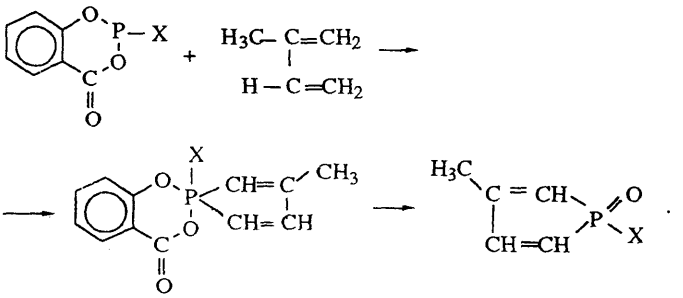
Exocyclic replacement of the chlorine atom in 1-Cl-BDPO also predominates in the reaction with alkylene oxides:[45]



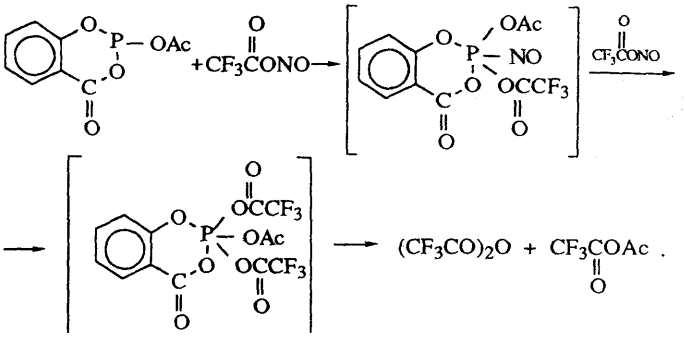
The reaction of this compound with amines is more complex. It involves not only the replacement of the chlorine atom but also splitting of the phosphorine ring:[16,46,47]



1-Chloro(ethoxy)-4,5-benzo-2,6-dioxaphosphorin-3-ones react with dienes. Their reaction with isoprene involves the intermediate formation of an unstable phosphorane, which when distilled is converted into 1-oxo-1-chloro(ethoxy)-3-methylphospholene:[48]



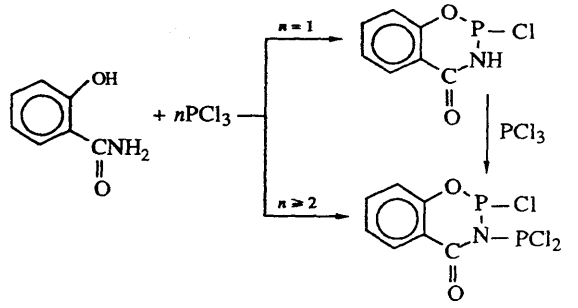
The reaction of BDPO with trifluoroacetyl nitrite gives the anhydride of trifluoroacetic acid and mixed anhydrides of trifluoroacetic acid and the acid whose residues was present on the phosphorus atom of the original phosphite:[49]



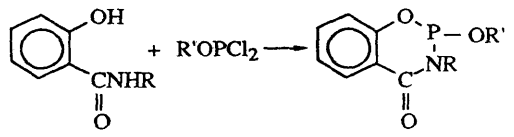
The structure of the phosphorus-containing product of this reaction has not been determined. The authors cited subsequently assigned to the organophosphorus compound formed the "general" structure $(R-COO)_3P=O$.[50]

b. 4,5-Benzo-2-aza-6-oxaphosphorin-3-ones and 4,5-benzo-6-aza-2-oxaphosphorin-3-ones

4,5-Benzo-2-aza-6-oxaphosphorin-3-ones (BAOPO) are obtained by the reaction of salicylamides with the chlorides of trivalent phosphorus acids. Salicylamides react with phosphorus trichloride in boiling benzene; the reaction is complete in several hours with the formation of a cyclic product,[51] and when there is a proton on the nitrogen atom this product can undergo further phosphorylation by an excess of phosphorus trichloride:[52]

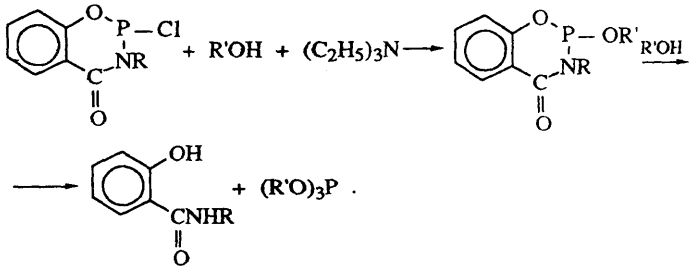


An analogous cyclisation is observed in the reaction of salicylamides with dichlorophosphites, which is complete with the formation of 1-alkoxy(phenoxy)oxa-azaphosphorin-3-ones:[51]

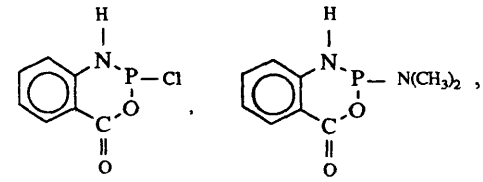


The reaction of salicylamides with amides of trivalent phosphorus acids takes place by an alternative route to give acyclic compounds[53] (see below).

1-Chloro-4,5-benzo-2-aza-6-oxaphosphorin-3-one (1-Cl-BAOPO) are highly reactive compounds. Their reactions with nucleophilic reagents can take place both with exocyclic replacement at the phosphorus atom and with splitting of the oxa-azaphosphorine ring. Thus 1-Cl-BAOPO reacts with stoichiometric quantity of an alcohol to give the 1-alkoxy-BAOPO, but in the presence of an excess of the alcohol the normal phosphite and the salicylamide are formed.[51]



Phosphorylated derivatives of anthranilic acid[54,55] with the general formula

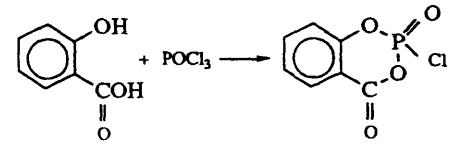


are structural isomers of 4,5-benzo-2-aza-6-oxaphosphorin-3-ones.

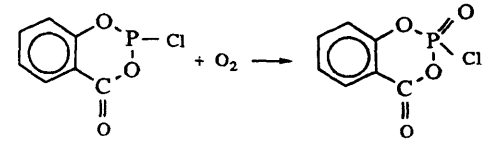
2. Cyclic phosphorus derivatives of salicylic acid containing a four-coordinate phosphorus atom

a. 4,5-Benzo-2,6-dioxaphosphorine-1,3-diones

A key intermediate in the synthesis of various 4,5-benzo-2,6-dioxaphosphorine-1,3-diones (BDPD) is 1-chloro-4,5-benzo-2,6-dioxaphosphorine-1,3-dione, for which several methods of preparation have been proposed. The simplest of these is based on the reaction of salicylic acid with phosphorus oxide chloride;[4,6,56,57]



The yield of 1-Cl-BDPD in this reaction does not exceed 50%; it can be obtained in higher yield by oxidising 1-Cl-BDPO with oxygen:[4,12]



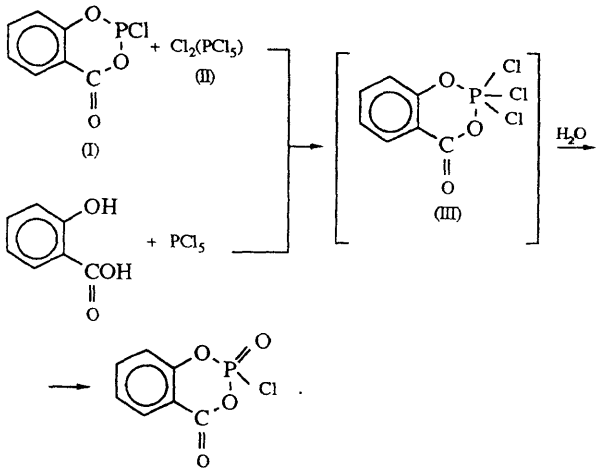
The phosphorus in 1-Cl-BDPO is only weakly nucleophilic, so that the addition of oxygen is slow, and the oxidation is not complete even on prolonged reaction.

1-Cl-BDPD, and also 1-fluoroalkoxy-derivatives of BDPD, were recently obtained in high yield (>90%) using trifluoroethyl sulphate as oxidising agent:[58]



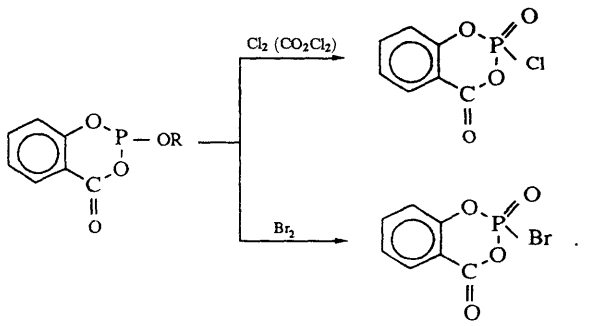
The addition of chlorine to 1-Cl-BDPO takes place more vigorously to give the trichlorophosphorane (III), controlled hydrolysis of which also gives 1-Cl-BDPO. The intermediate

phosphorane (III) can be obtained by the reaction of salicylic acid or 1-Cl-BDPO with phosphorus pentachloride:[12,59,60]



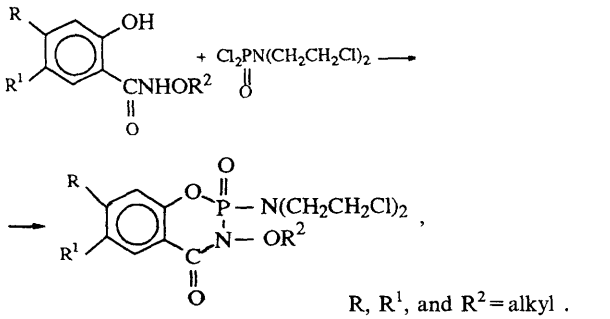
It was subsequently shown, however, that stable intermediate phosphoranes of type (III) are not formed in the reaction of the phosphite (I) with phosphorus pentachloride and chlorine.[61] The formation of stable products was observed only in the reactions of 1-chloro-4,5-benzo-2-phenylaza-6-oxaphosphorin-3-one and its 1-phenoxy analogue with chlorine.[62]

1-Cl-BDPD and 1-Br-BDPD are formed by the reaction of 1-alkoxy-BDPO with chlorine (sulphuryl chloride) or bromine respectively:[30,33]



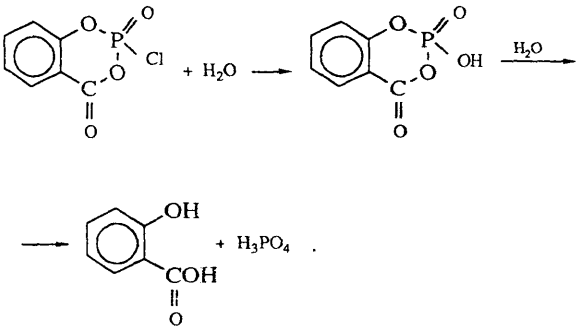
When the reaction with bromine is carried out under controlled conditions at a low temperature, ring opening takes place initially to give a product which undergoes cyclisation when the temperature is increased.[33] A similar result was obtained in a study of the reaction of 1-Cl-BDPO with halogens.[63]

Phosphorylation takes place with amidodichlorophosphates and hydroxamic derivatives of salicylic acid:[64]

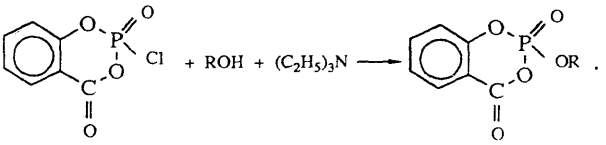


R, R^1, and R^2 = alkyl .

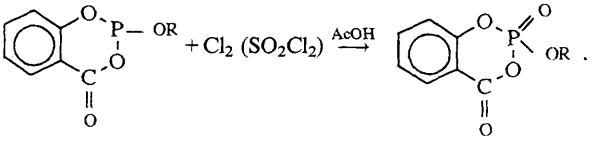
The reaction of 1-Cl-BDPD with nucleophilic reagents may involve both replacement of the chlorine atom and splitting of the phosphorine ring. On careful hydrolysis of 1-Cl-BDPD, replacement of chlorine by a hydroxyl group has been observed, but the resulting 1-hydroxy-4,5-benzo-2,6-dioxaphosphorinic acid is extremely unstable and is rapidly hydrolysed to give phosphoric and salicylic acids:[65]



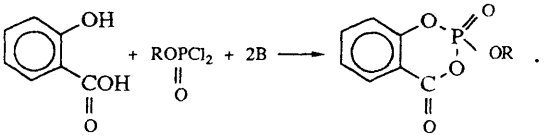
The replacement of chlorine by alkoxy and aryloxy groups takes place more selectively in the presence of hydrogen chloride acceptors to give 1-alkoxy(aryloxy)-4,5-benzo-2,6-dioxaphosphorine-1,3-diones;[6,66–68] the reaction takes place by an $S_N2(P)$ mechanism:[69]



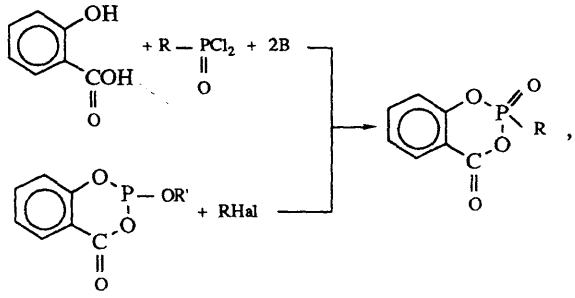
1-Chloroalkoxy(aryloxy)-BDPD have been synthesised by the reaction of 1-chloroalkoxy(aryloxy)-BDPO with chlorine or sulphuryl chloride in the presence of acetic acid:[30]

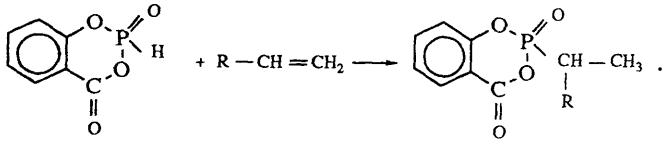


1-Alkoxy(aryloxy)BDPD have also been obtained by the counter cyclisation of the corresponding dichlorophosphates with salicylic acid:[70]



Dichlorides of phosphonic acids undergo similar cyclisation to give 1-alkyl(aryl)-BDPD, which can also be obtained by the Arbuzov[29,57,71] and Pudovik[43] reactions:



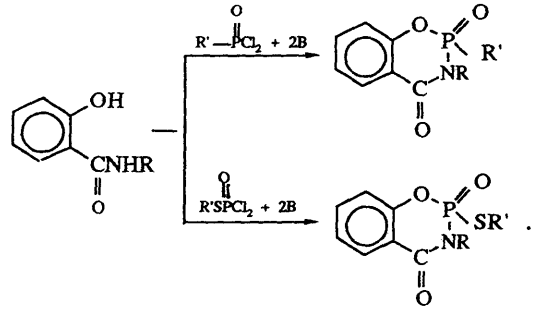


$R = C_6H_5$, C_2H_5, C_6H_5O, C_2H_5O

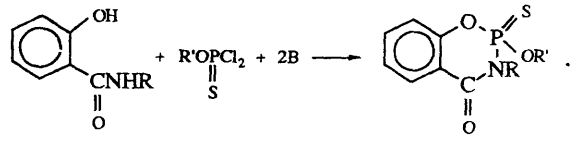
In the last case a rare non-catalysed electrophilic version of the reaction takes place.

b. **4,5-Benzo-2-aza-6-oxaphosphorine-1,3-diones and 4,5-benzo-2,6-diazaphosphorine-1,3-diones**

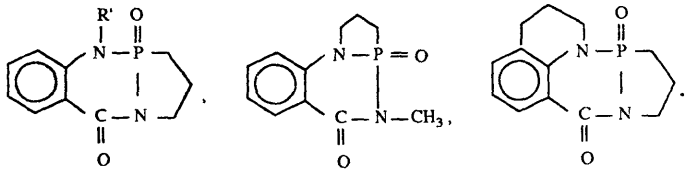
The reaction of the dichlorides of alkylphosphonic acids and alkyl dihydrogen thiophosphates with salicyliamides has been used to synthesise 1-alkyl(thioalkyl)-4,5-benzo-2-aza-6-oxaphosphorine-1,3-diones:[72–74]



The thione isomers were synthesised by the reaction of salicylamides with alkyl thiodichlorophosphates:[75]

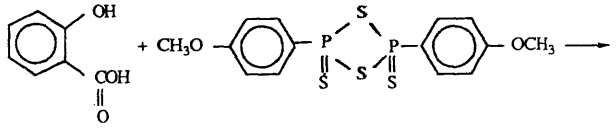


Unusual directions of the cyclisation were observed[76,77] for phosphorylated salicylamides containing a 3-chloropropyl substituent on the phosphorus or nitrogen atoms:

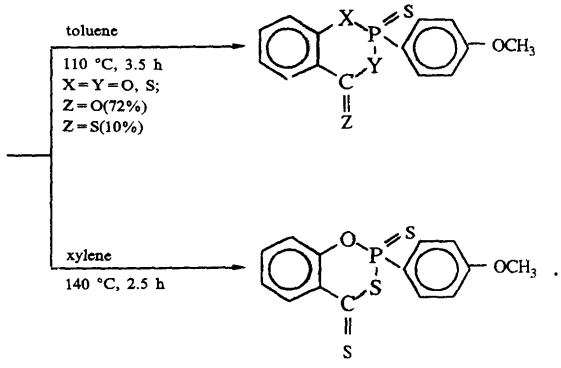


c. **1-Thio-4,5-benzo-2,6-X,Y-phosphorin-3-ones (thiones)**

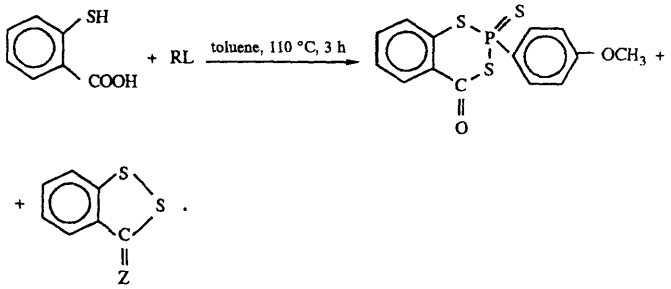
Thiophosphorus derivatives of salicylic acid have been obtained using Lawesson's reagent (RL).[78] The direction of the reaction of salicylic acid with Lawesson's reagent depends on the temperature and the solvent:



(RL)

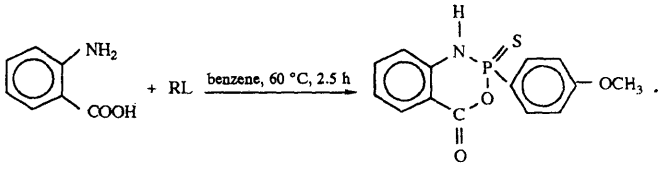


In the analogous reaction of α-mercaptobenzoic acid, phosphorylation and thionation of the original acid take place:



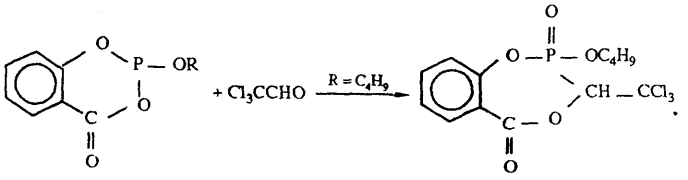
Z = O (15%); Z = S (52%) .

The reaction of anthranilic acid with Lawesson's reagent leads to only phosphorylation:

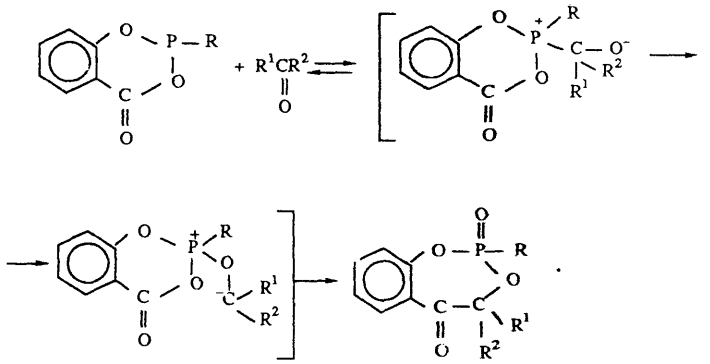


d. 5,6-Benzo-4-oxo-3,7-dioxa-1-phosphepines and 5,6-benzo-4-oxo-2,7-dioxa-1-phosphepines

An interesting feature of the reactivity of BDPO was revealed in the reactions with carbonyl compounds, in which expansion of the ring to give a phosphepine ring was observed:[79]



For R = CH_2CF_3 and $CH_2(CF_2)_2H$ the reactions were much slower, but had a high stereoselectivity, reching 95%.[80] When hexafluoroacetone and ethyl pyruvate were taken for the reaction, the expansion of the ring was accompanied by P–C → P–O–C rearrangement to give a new C–C bond:[81–83]



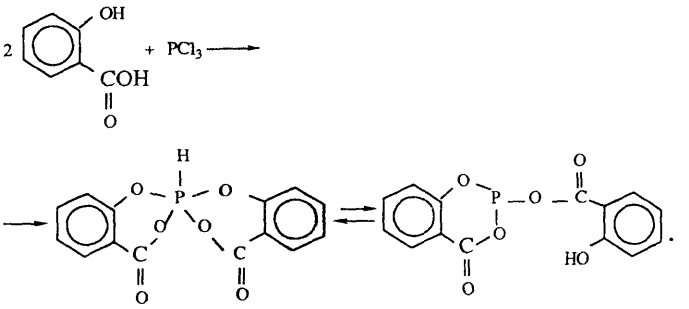
R = $N(C_2H_5)_2$, OC_2H_5, OCH_2CF_3, $OCH_2(CF_2)_2H$, $OCH_2P(O)(OC_2H_5)_2$;

$R^1, R^2 = CF_3$, CH_3, $COOC_2H_5$.

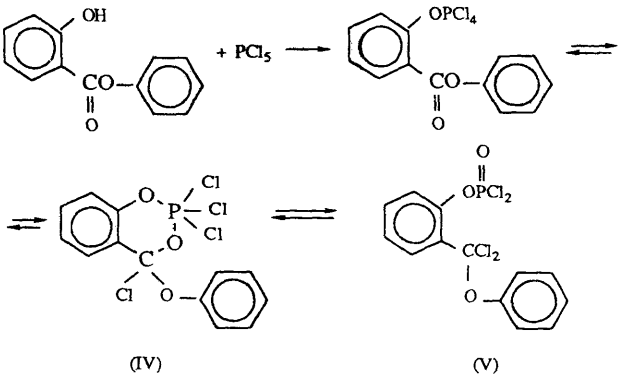
An analogous synthetic result was obtained with methyl trifluoropyruvate.[84]

3. Phosphorus derivatives of salicylic acid containing a five-coordinate phosphorus atom

The reaction of phosphorus trichloride with an excess of salicylic acid gives not 1-Cl-BDPO but a bicyclic phosphorane in equilibrium with its monocyclic form;[14,85] no ^{31}P NMR data have been published, however.



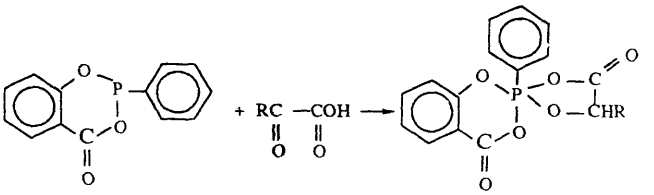
The reaction of phenyl salicylate with phosphorus pentachloride gives the monocyclic phosphorane (IV),[86] but its structure also has not been proved. The conversion of compound (V) into compound (IV) appears doubtful.



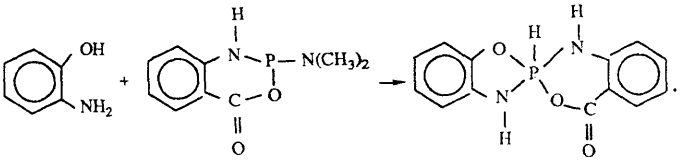
(IV) (V)

The formation of a phosphorane structure has also been assumed to take place in the careful hydrolysis of salicyl phosphate.[87] Phosphorane derivatives of salicylic acid are extremely reactive and have been little studied, and for the most part their structures have been only postulated.[60,69,87]

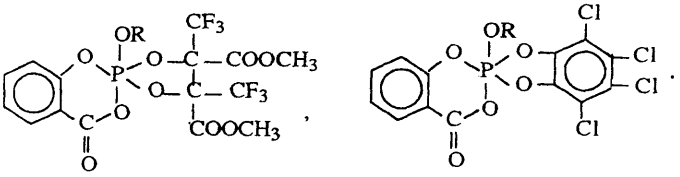
Spirodiacyloxyphosphoranes have been obtained by the reaction of 1-phenyl-BDPO with α-ketoacids, acrylic acid, and β-propiolactone, and their formation has been proved by ^{31}P NMR:[88]



A spirocyclic P–H-phosphorane based on anthranilic acid and *ortho*-aminophenol has been obtained, and its structure proved by ^{31}P NMR (δ_P 59 p.p.m., $^1J_{P-H}$ 860 Hz).[55]

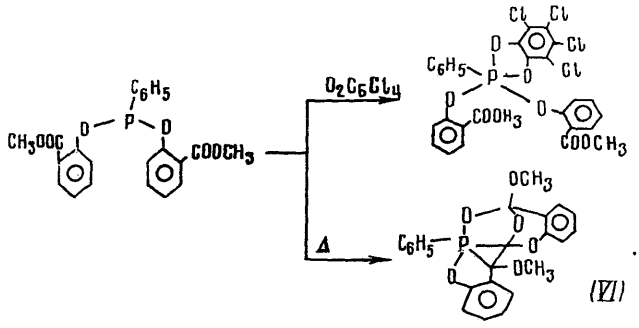


Spirobicyclic phosphoranes are also formed in the reactions with methyl trifluoropyruvate,[84] benzil, *ortho*-chloranil,[89] and phenyl azide:[83]



R = CH_2CF_3, $CH_2(CF_2)_2H$.

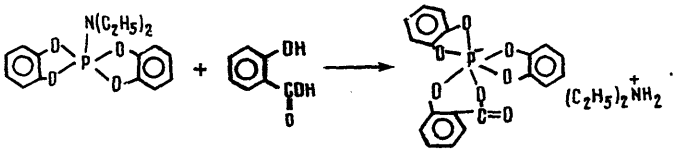
A compound of five-coordinate phosphorus has also been obtained by the reaction of an acyclic bis(2-methoxycarbonylphenyl) phosphonite with *ortho*-chloranil:[90]



(VI)

With heating, the phosphonite undergoes an unusual cyclisation to give the tricyclic phosphorane (VI).

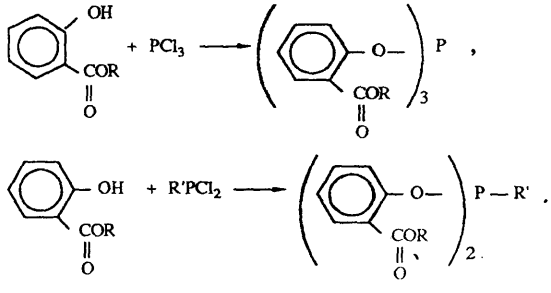
We detected the only example of a six-coordinate structure, containing a salicylate ring and obtained from diethylaminobis-(pyrocatecholato)phosphorane and salicylic acid:[91]



III. Acyclic phosphorus-containing derivatives of salicylic acid

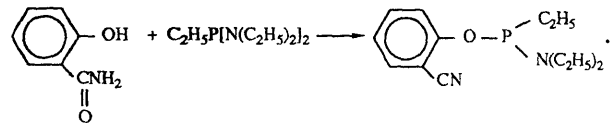
1. Acyclic phosphorus derivatives of salicylic acid containing a three-coordinate phosphorus atom

Esters of salicylic acid, like phenols, are phosphorylated at the hydroxyl group. Thus they react with phosphorus trichloride to give 2-alkoxycarbonylphenyl phosphites, and with dichlorophosphines to give the phosphonites:[92]

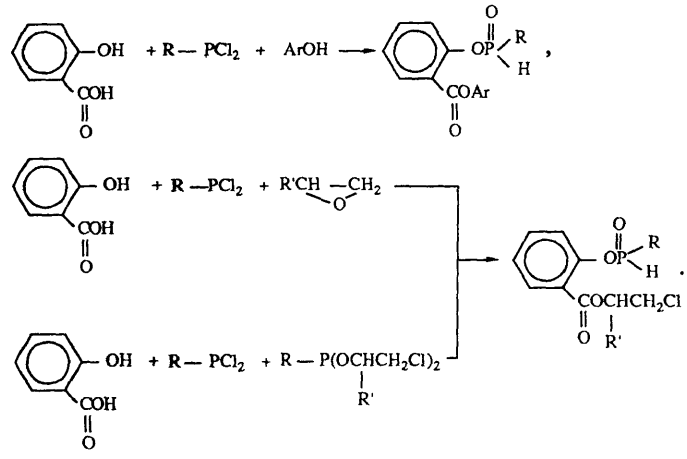


The data[92] on the synthesis of the phosphonites were later refuted[90] (see above), and it was possible to obtain these phosphonites only using bases.

Salicylamides react with phosphorus trichloride and dichlorophosphites to give mainly cyclic products,[51,52] and acyclic compounds were obtained only in the reaction with diamidophosphonites; in the opinion of the authors cited, this is due to the previous dehydration of the carbamoyl fragment of the salicylamide:[53]



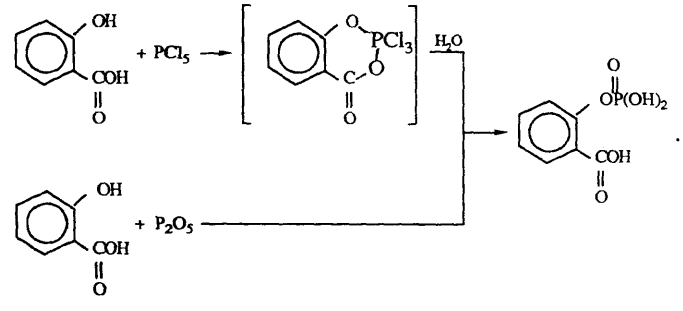
Acid esters of phosphonous acid have been synthesised by the reactions of the corresponding phosphorus chlorides with salicylic acid in the presence of phenols or alkylene oxides,[93,94] and also by an exchange reaction:[95]



2. Acyclic phosphorus derivatives of salicylic acid containing a four-coordinate phosphorus atom

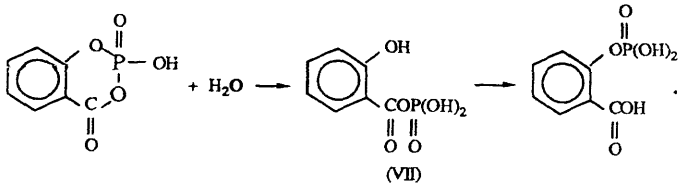
a. Phosphates and phosphonates

Phosphorylsalicylic acid is an analogue of acetylsalicylic acid, but it has not been used in medicine. Phosphorylsalicylic acid can be obtained by the direct phosphorylation of salicylic acid, and also from its cyclic phosphorus derivatives. The most convenient method of obtaining phosphorylsalicylic acid is based on the successive reactions of salicylic acid with phosphorus pentachloride and water.[59,60,61,87,96] Phosphorus pentoxide can also be used as phosphorylating agent:[97]



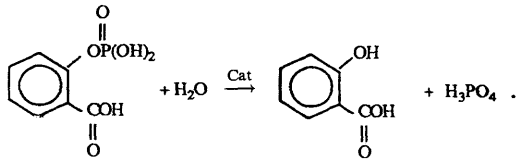
The hydrolysis of the cyclic salicylphosphoric acid to phosphoryl-salicylic acid has been said to take place via the formation of the mixed anhydride (VII),[65] but this appears doubtful, since anhydride

bonds are hydrolysed much more readily.[8] The hydrolysis of acyl phosphates, including salicyl phosphates, has been reviewed briefly.[98]



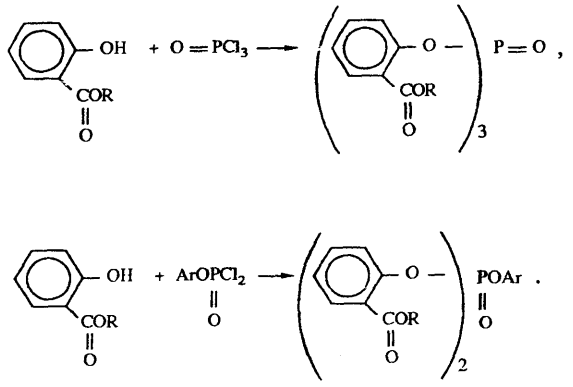
(VII)

Phosphorylsalicylic acid readily undergoes further hydrolytic splitting to give phosphoric and salicylic acids.[99–104] Hydrolysis takes place more readily in a neutral medium, and is slower in strongly acidic and alkaline media.[105] The hydrolysis is catalysed by calcium ions, glyceryl phosphate, and bovine phosphatase; the hydrolysis of phosphorylsalicylic acid by bovine phosphatase is twice as rapid as that by glyceryl phosphate.[102–104]

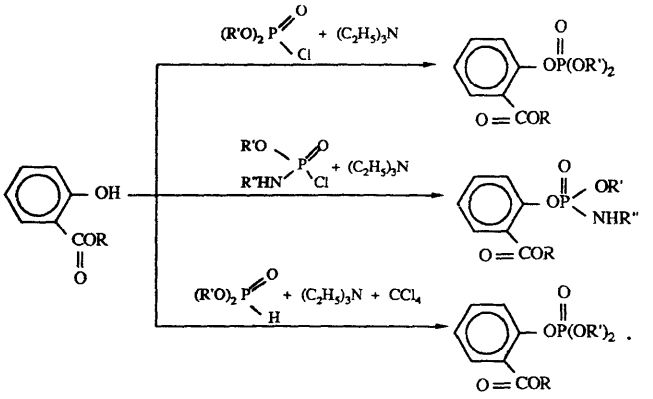


A large number of salicyl phosphates and phosphonates have been obtained in the search for biologically active substances and technically important compounds.

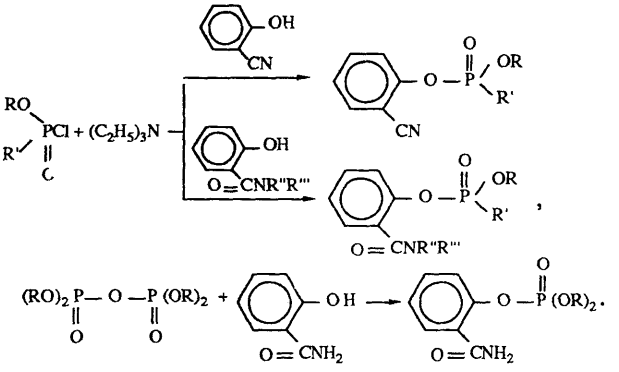
The reaction of salicylate esters with phosphorus oxide chloride or aryl chlorophosphates and chlorophosphonates[106,107] has been used to synthesise aromatic esters of salicylphosphoric and -phosphonic acids, proposed as polymer stabilisers:[106,107]



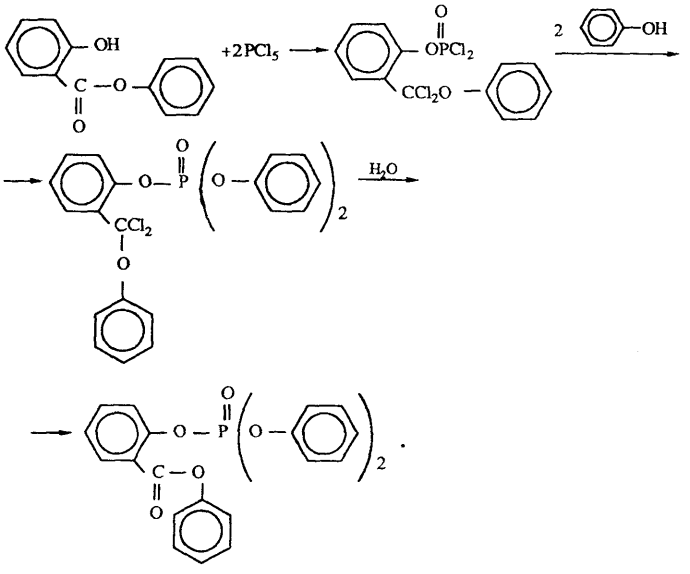
The phenolate of salicylic acid is weakly nucleophilic, and is phosphorylated by halides of phosphorus acids with difficulty.[108] Esters of salicylic acid in the presence of bases, however, are readily phosphorylated by dialkyl chlorophosphates[107–111] and amidochlorophosphates[109] to give 2-alkoxycarbonylphenyl esters of phosphorus acids, some of which are interesting insecticides and acaricides.[112] These compounds were obtained by the Todd–Atherton reaction:[113]



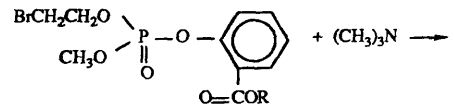
Substances with fungicidal activity have been synthesised by the reaction of salicylonitriles[114,115] and salicylamides[116] with dialkyl chlorophosphates. With salicylamides, pyrophosphates have also been used:[117]

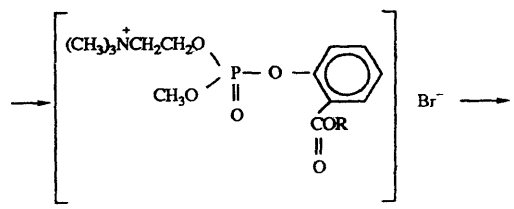


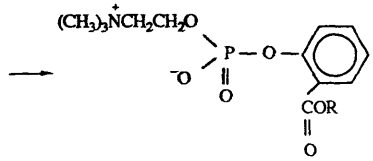
An extremely original method has been proposed for synthesising phosphorylsalicylic acid, based on the successive reactions of aryl esters of salicylic acid with phosphorus pentachloride, phenol, and water:[118]



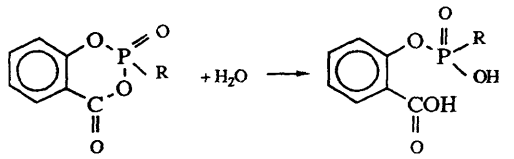
Aliphatic esters of salicylphosphoric acid can undergo dealkylation, and this has been used to synthesise salicyl phosphoxolines:[119]



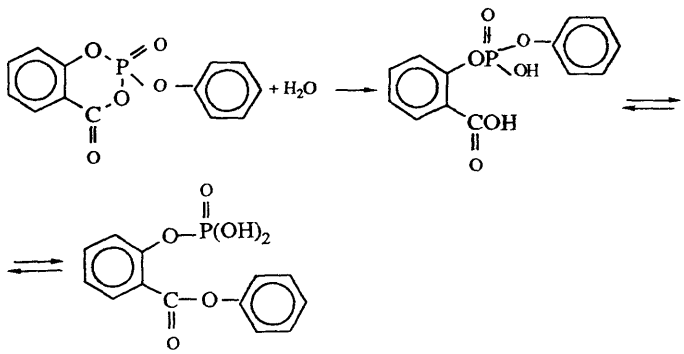




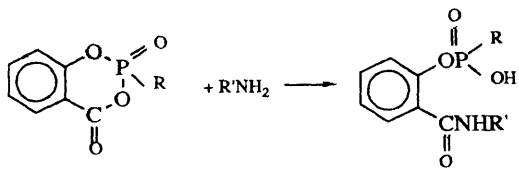
Acid esters of salicylphosphoric and -phosphonic acids are conveniently obtained by the hydrolysis of cyclic salicyl phosphates (BDPD):[68,120]



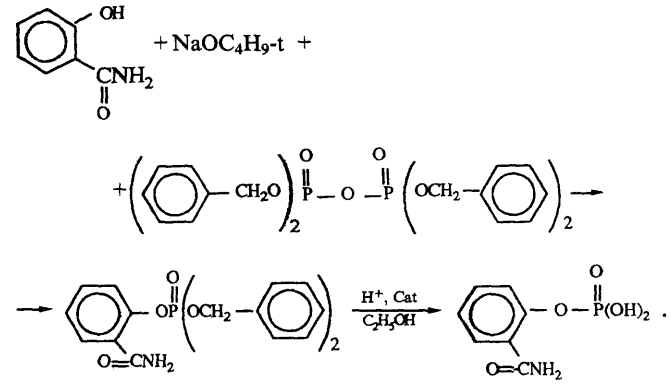
An interesting feature is that in aromatic acid esters of this type, migration of the aryloxy-group between the phosphoryl and the carboxyl groups has been observed:[65,121]



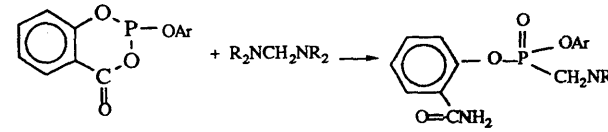
The reaction of 1-alkyl(aryl)-BDPD with amines gives 2-carbamoylphenyl esters of alkyl(aryl) hydrogen phosphates and alkyl(aryl) hydrogen phosphonates:[66,67,69,122]



Phosphorylation of salicylamide by tetrabenzyl pyrophosphate followed by hydrolysis of the dibenzyl 2-carbamoylphenyl phosphate obtained gives 2-carbamoylphenyl phosphate:[123]

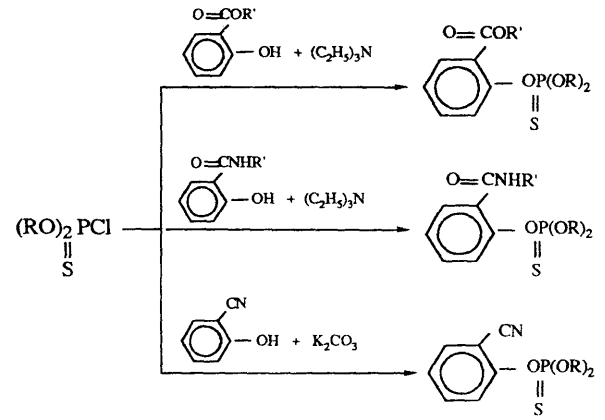


The reaction of 1-aryloxy-4,5-benzo-2,6-dioxaphosphorin-3-ones with bis(dialkylamino)methane, which gives O-aryl O-(2-carbamoyl)-phenyl aminomethylphosphonates, may be of interest:[124]



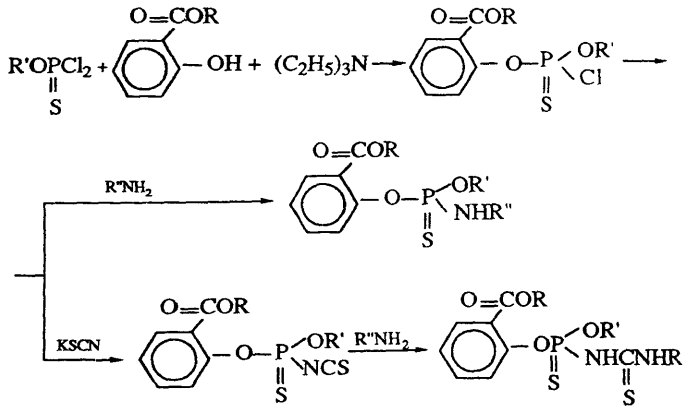
b. Derivatives of thiophosphorylsalicylic acid

The sulphur-containing phosphorus derivatives of salicylic acid include compounds with thione and thiol sulphur on the phosphorus atoms. Compounds containing sulphur in the salicylic acid fragment have not been described. The thione isomers have been synthesised mainly by the reactions of the chlorides of phosphorus thio-acids with derivatives of salicylic acid. Thus the reaction of dialkyl thiochlorophosphates with esters,[125] amides,[126,127] and nitriles[125,128–130] of salicylic acid in the presence of hydrogen chloride acceptors has been used to obtain the corresponding *ortho*-substituted phenyl esters of dialkyl hydrogen thiophosphates, which have insecticidal activity:[125–130]



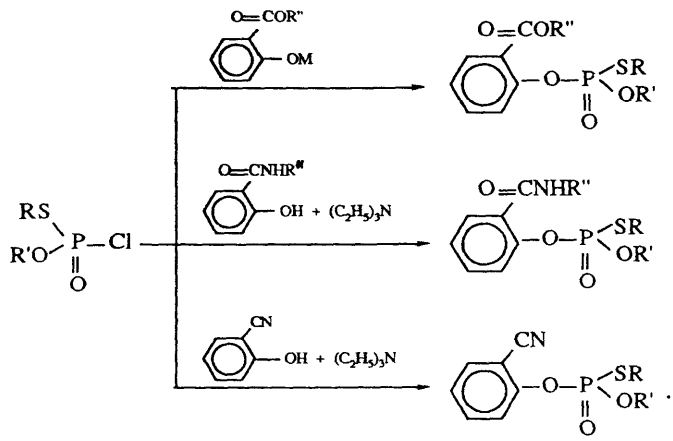
Esters,[131] amides,[126,132,133] and nitriles[134,135] of salicylic acid in the presence of hydrogen chloride acceptors also react with the ester chlorides of alkyl(aryl) hydrogen thiophosphonates to give the *ortho*-substituted phenyl esters of thiophosphonic acids, with insecticidal activity.[131–136]

An interesting feature is that in the reaction of alkyl thionodichlorophosphates with esters of salicylic acid, selective replacement of one chlorine atom by an alkoxycarbonylphenoxy-group is possible, and this has been used to synthesise amide esters[137–142] and thioureide esters[143] of thiophosphorylsalicylic acid:

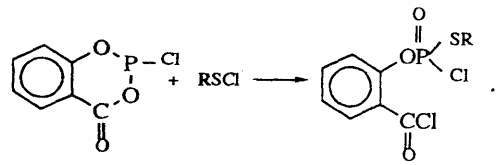


A fairly extensive group is formed by the thiol derivatives of phosphorylsalicylic acid, which are now being studied intensively in the search for pesticides with a low toxicity towards warm-blooded animals.[144–157]

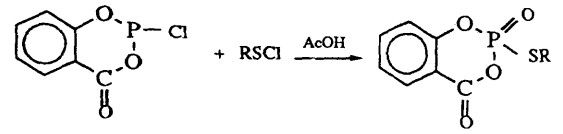
Esters,[144–151] amides,[147,152] and nitriles[153,154] of salicylic acid in the presence of hydrogen chloride acceptors react with thiolochlorophosphates to give thiol derivatives of phosphoryl-salicylic acid, many of which have been patented as insecticides and acaricides.[144–156]



An extremely interesting method of attaching a thiol group to a phosphorus atom is based on the splitting of the phosphorine ring in 1-Cl-BDPO by sulphenyl chloride to give the dichlorides of thiolo-phosphorylsalicylic acid,[158] which can be used as intermediates in the synthesis of biologically active substances:



The view that in the presence of acetic acid the reaction of 1-Cl-BDPO with sulphenyl chlorides takes place with preservation of the phosphorine ring[158] apparently requires confirmation.



* *
*

The analysis of published material shows that phosphorus-containing derivatives of salicylic acid represent an extensive group of cyclic and acyclic multidentate compounds, whose chemistry is now being intensively developed. The further development of the chemistry of acyclic phosphorus derivatives of salicylic acid is of undoubted interest in the search for new physiologically active substances.

Cyclic phosphorus derivatives of salicylic acid are highly reactive and of considerable interest as valuable synthons. The chemistry of some types of cyclic phosphorus derivative of salicylic acid has still been little studied, however. Thus there are very few data on salicyl-containing phosphoranes or proofs of their structure, although these compounds are of interest for chemical theory and as synthetic intermediates.

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Received 17th March 1992