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Methods of Synthesis of Arylphosphonic and Arylphosphonothioic Acids and Their Derivatives

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A systematic account is given of data on the synthesis of arylphosphonic and arylphosphonothioic acids and their derivatives by the addition of oxygen or sulphur to arylphosphonous acids, their esters, amides, and dihalides, by treating phosphoryl chloride, dialkyl phosphorochloridates, and phosphorodiamidic chlorides with aryl-substituted organometallic compounds, by the reaction of benzene and its derivatives containing various substituents in the ring with phosphorus pentoxide, phosphorus sulphide halides, phosphorus sulphides, and esters of phosphorous and phosphorothious acids, and by other less familiar methods. The methods of synthesis of aryldihalogenophosphines, which are important intermediates in the synthesis of arylphosphonic acids and their derivatives, are described.
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I. INTRODUCTION

By virtue of the wide variety of their properties due to the presence of two reaction centres, namely the aromatic ring and the phosphono-group, and also as a consequence of the various aspects of their possible practical applications which have been discovered, aryl phosphonic acids and their derivatives have been the subject of numerous investigations. At present there exist extensive data on this question in both Soviet and foreign literature, but there have been no surveys with the exception of two published in 1957–1958 in which the data accumulated were only partly utilised.[1,2] This review deals with data on the methods of synthesis of arylphosphonic and arylphosphonothioic acids and their derivatives which have been published up to the middle of 1984.

II. METHODS OF SYNTHESIS OF ARYLPHOSPHONIC ACIDS AND THEIR DERIVATIVES

Arylphosphonic acids and their derivatives are obtained by various procedures which can be divided into two groups. The first group includes methods based on the oxidation of arylphosphonous acids and their derivatives and the second includes methods which lead to the formation of a phosphorus–carbon bond.

1. Oxidation of Arylphosphonous Acids and Their Derivatives

Apart from the oxidation of arylphosphonous acids and their salts, esters, amides, and chlorides, this Section also includes the reactions of α-chlorocarbonyl compounds with arylphosphonites. Arylphosphonous acids and their salts, esters, and amides are oxidised by oxygen,[3-5] hydrogen peroxide,[3,6] manganese dioxide,[7] calomel,[8] nitric acid,[9,10] and chlorine[11,12] to phosphonic acids and their derivatives. The reaction of the esters and ester imides of arylphosphonous acids with chloral leads to derivatives of arylphosphonic acids containing the dichlorovinyl group in the ester moiety in yields up to 79.5%:[13-15]

$$R^1C_6H_4P(OR^2)(XR^2) + OCHCCl_3 \rightarrow R^1C_6H_4(O)P(OCH{=}CCl_2)XR^2\ ;$$
$$R^1{=}H, Cl;\ R^2 = C_1\text{-}C_4\ alkyl,\ (CH_2CH_2O)_2CH_3;\ X{=}O, NCH_3\ .$$

Various derivatives of chloroacetoacetic acid react similarly with arylphosphonites:[16]

$$R^1C_6H_4P(OR^2)_2 + R^2C(O)CHClCOOC_2H_5 \rightarrow$$
$$\rightarrow R^1C_6H_4(O)P(OCR^2{=}CHCOOC_2H_5)OR^2\ ;$$
$$R^1{=}H, CH_3, C_2H_5, N(CH_3)_2, N(CH_3)C_6H_5, NO_2;\ R^2 = C_1\text{-}C_4\ alkyl.$$

Aryldihalogenophosphines are oxidised by oxygen,[17-19] chlorine or bromine in t-butyl alcohol,[20] chlorine with subsequent treatment of the reaction mixture with sulphur dioxide,[21-26] acetals[27] or ketones,[28] chlorine in the presence of phosphorus pentoxide,[29-31] and sulphuryl chloride[29,32-35] with formation of arylphosphonic acid dichlorides in yields of 70–98%. Aryl dihalogenophosphines in the form of aluminium chloride complexes can be used in the oxidation reaction. In certain cases the oxidised complex is esterified with an excess of alcohol and then subjected to acid hydrolysis.[36-42]

The dichloride of phenylphosphonic acid is obtained also by the reaction of the thioanhydride of phenylphosphonothious acid with sulphuryl chloride[43] or by the successive treatment of phenylphosphonothioic dichloride (and also its mixture with phenylphosphonic acid) with chlorine and sulphur dioxide.[44,45]

2. Methods of Synthesis of Aryldihalogenophosphines

All the derivatives of arylphosphorous acids enumerated in the previous Section are usually obtained from aryldihalogenophosphines,[3] the main methods of synthesis of which are considered in this Section.

(a) Arylation of Phosphorus Halides by Aromatic Hydrocarbons

At a temperature above 550 °C benzene interacts with phosphorus pentachloride, the degree of conversion of which into dichlorophenylphosphine for a phosphorus pentachloride : benzene molar ratio of 1 : 14 reaches 8%.[19] Dichlorophenyl- and dichlorotolyl-phosphines are formed when benzene or toluene interacts with phosphorus trichloride at 500–600 °C.[46-52] The yield of dichlorophosphines reaches 70–99% when the reaction is carried out in the presence of

catalysts: oxygen,[53] alkyl halides,[54] phosgene,[55] or zeolites.[56–58] When anhydrous aluminium chloride is used as the catalyst, the phosphorylation temperature is reduced to 60–80 °C. Aryl dichlorophosphines with a small admixture of diarylchlorophosphines are obtained in the form of complexes with aluminium chloride:[36,59–61]

$$ArH + PCl_3 + AlCl_3 \rightarrow ArPCl_2 \cdot AlCl_3 + HCl \ .$$

Equimolar ratios of the aromatic hydrocarbon and aluminium chloride are usually employed with a not less than a threefold excess of phosphorus trichloride, because otherwise the amount of the diarylchlorophosphine impurity increases sharply. The reaction time varies from 1 to 8 h. After more prolonged refluxing (36 and more hours), the content of diarylchlorophosphines rises to 30% and more.[36]

Aryldichlorophosphines are isolated from the complex by treatment with phosphoryl chloride,[21,62–64] pyridine,[65,66] phosphoric acid, tri(2-chloroethyl)phosphate,[67–69] ethers and esters, ketones,[70] or the calculated amount of water.[64,71] After the decomposition of the complex, the aryldichlorophosphine is extracted with benzene,[67] petroleum ether,[9,64,72] or phosphorus trichloride[63,73] and is isolated by distillation.

The method is convenient in laboratory practice and has been tested on an experimental apparatus in the synthesis of dichlorophenyl- or dichloro-4-tolyl-phosphines.[74] It makes it possible to obtain aryldichlorophosphines containing one or several substituents in the ring. Thus, when phosphorus trichloride interacts with benzene, toluene, ethylbenzene, xylene, 1,2-diphenylethane, and diphenylmethane, dichlorophenyl-,[9,10,21,23,36,63–70,74–79] dichlorotolyl-,[21,40,73,74,80] dichloroethylphenyl-,[21,40,62,81,82] dichloroxylyl-,[77,78,80,81,83,84] dichloro(4-phenylethylphenyl)-,[80] and 4-benzylphenyldichloro-phosphines[80,85,86] are formed respectively. When biphenyl and bidenzofuran are used, the corresponding mono- and bis-dichlorophosphines are formed depending on the reactant ratio.[80,86–88]

When alkylbenzenes (RC_6H_5) are phosphorylated, the yield of aryldichlorophosphines ($RC_6H_4PCl_2$) diminishes with increase of the length of the alkyl group from 60–89% for $R = CH_3$ or C_2H_5 to 33–39% for $R = C_4H_9$.[21] The phosphorylation of monoalkylbenzenes always leads to a mixture of isomeric dichlorophosphines. For example, dichlorotolylphosphine is a mixture of the 4-, 3-, and 2-isomers in proportions of 63 : 27 : 10 and dichloroethylphenylphosphine is a mixture of the 4- and 3-isomers.[40,81] The methyl groups in the dichlorophosphine prepared from *p*-xylene are in the 2- and 5-positions,[81] while in the case of *o*-xylene the product is dichloro-3,4-dimethylphenylphosphine.[84] When trifluoromethanesulphonic acid is used instead of aluminium trichloride, the yield of dichloro-3,4-dimethylphenylphosphine is 33%.[89] The phosphorylation of pseudocumene and mesitylene leads to the formation of the corresponding dichlorophosphines in 45% yield,[90,91] while phosphorylation of the symmetrical tri-t-butylbenzene gives rise to the corresponding phosphines in 71% yield.[92] Alkylbenzenes containing a silicon atom in the side chain are phosphorylated to aryldichlorophosphines, the yield of the mixture of 4- and 2-isomers amounting to 32–52%:[93,94]

$$Cl_n(CH_3)_{3-n}Si(CH_2)_m C_6H_5 + PCl_3 \xrightarrow{AlCl_3} Cl_n(CH_3)_{3-n}Si(CH_2)_m C_6H_4PCl_2 ;$$
$$n, m = 1-3 \ .$$

Aryl halides are also phosphorylated: on being refluxed with phosphorus trichloride and aluminium chloride, fluorobenzene affords dichloro-4-fluorophenylphosphine in 45 to 65% yield,[24,95–97] while chlorobenzene gives rise to a mixture of the isomeric chlorophenyldichlorophosphines in yields up to 80%,[36,63,73,81,98–100] the 4-isomer predominating.[34,97,101] When bromobenzene is phosphorylated, the yield of 4-bromophenyldichlorophosphine varied from 14 to 51%, depending on the reaction conditions,[23,72,73,97] while the yield of the 2-bromoisomer is 41.5%.[32] 3-Chloro-4-tolyldichlorophosphine has been obtained from 2-chlorotoluene in 10–15% yield.[22]

After 1,2- and 1,4-dichlorobenzenes have been refluxed for a long time with phosphorus trichloride and aluminium chloride, the products are respectively 3,4- and 2,5-dichlorophenyldichlorophosphines which were identified in the form of arylphosphonic acids; the yield of products is then appreciably lower than in the case of chlorobenzene, while trichlorobenzenes do not undergo the phosphorylation reaction at all.[36]

The polyfluorobenzenes C_6HF_4R with $R = NO_2$ and CH_2SO_2 do not undergo the phosphorylation reaction, the phosphorylation of derivatives with $R = OCH_3$ and SCH_3 is accompanied by the dissolution of the ester linkage, while compounds with R = H, F, or CF_3 produce dichlorophosphines in yields of 37–53%.[102]

The alkyl esters or thioethers of monohydric and dihydric phenols are phosphorylated by phosphorus trichloride in the presence of aluminium, iron, and zinc chlorides with formation of 4-alkoxyphenyldichlorophosphines in yields not exceeding 39%,[23,72,80,103–106] while in the presence of stannic chloride the yield is 26–91%:[107,108]

$$R^1R^2R^3C_6H_3 + PCl_3 \rightarrow R^1R^2R^3C_6H_2PCl_2$$
$$R^1 = H, C_1-C_4 \text{ alkyl}; \ R^2 = OR^1, SCH_3; \ R^3 = H, CH_3, OCH_3 \ .$$

When the dimethyl ether of resorcinal was phosphorylated in the presence of iron(III) chloride, dichloro-2,4-dimethoxyphenylphosphine was obtained in 27% yield,[109] when zinc chloride in a proportion not more than 0.06 mol per mole of the ether was used, the yield of the aryldichlorophosphine was 69%, while in the presence of an equimolar amount of zinc chloride only tris(2,4-dimethoxyphenyl)phosphine was formed in 14% yield.[35,103]

Diphenyl ether reacts with phosphorus trichloride and aluminium chloride, taken in molar proportions of 1 : 1 : 0.15, and gives rise to dichloro-4-phenoxyphenylphosphine in 13.7% yield.[110]

When 2,3-benzo-1,4-dioxan is heated with phosphorus trichloride and a catalytic amount of zinc chloride, the aromatic ring is phosphorylated in the *meta*-position, the yield of the corresponding dichlorophosphine being 50%.[111]

The phosphorylation of *NN*-dialkylanilines with phosphorus trichloride takes place in the absence of a catalyst, the yield of 4-*NN*-dialkylaminophenyldichlorophosphines amounting to 60–97%.[23,112,113] The presence of aluminium chloride reduces the yield to 36%.[8,114,115]

Aryldibromophosphines are obtained by heating aryldichlorophosphines with phosphorus tribromide or with gaseous hydrogen bromide.[97]

Dichlorophenylphosphine is obtained by heating a mixture of chlorodiphenyl- or triphenylphosphine with phosphorus trichloride to 350 °C.[116,117]

(b) Arylation of Phosphorus Trihalides by Organometallic Compounds

Various aryldichlorophosphines have been synthesised by this method from diarylmercury;[3,8,48,80,118] for example, dichloro-2-tolylphosphine has been obtained in 78% yield:

$$Hg(C_6H_4R)_2 + 2PCl_3 \xrightarrow{130-230^\circ} 2RC_6H_4PCl_2 + HgCl_2 \ ;$$
$$R = H, Cl, CH_3, OCH_3, N(CH_3)_2 \ .$$

Dichlorophenyl-, dichloro-2-tolyl-, dichloro-4-tolyl-, and dichloro-4-ethylphenyl-phosphines have been obtained by heating phosphorus trichloride with the corresponding aryl-

zinc bromide (yields up to 32%) and 4-bromophenyldichlorophosphine has been obtained in a yield of 8%.[119,120] Dichloro-4-trifluoromethylphenylphosphine has been synthesised analogously.[25] When tetraphenyl-lead or tetraphenyl–tin is heated for a long time (180 h) with phosphorus trihalide, the yield of the dihalogenophenylphosphines reaches 93%,[121,122] while in the case where triphenyl–antimony and bismuth are used the yield is much lower.[123,124]

Aryldichlorophosphines, aminoarylchlorophosphines, and arylphosphonous acid amides have been obtained in yields of 32–85% by the reaction of arylmagnesium bromides with phosphorus trichloride.[102,125–127] On treatment with hydrogen chloride, the amides of arylphosphorous acids are readily converted into aryldichlorophosphines:[128]

$$(R^1_2N)_n PCl_{3-n} + ArMgBr \rightarrow (R^1_2N)_n P(Ar)Cl_{2-n} \xrightarrow{HCl} ArPCl_2 ;$$
$$R^1 = CH_3, C_2H_5; Ar = 2\text{-}BrC_6H_4CH_2C_6H_5, 2\text{-}, 3\text{-} \text{ or } 4\text{-}FC_6H_4, 4\text{-}R^2C_6F_4; R^2 = H, F, Cl, CF_3, OCH_3; n = 0-2 .$$

o-Phenylenebis(tetramethyldiaminophosphine) has been obtained in 84% yield by the reaction of (tetramethyldiamino)-2-lithiophenylphosphine with chloro(tetramethyldiamino)phosphine; on treatment with hydrogen chloride, the product is converted into *o*-phenylenebis(dichlorophosphine).[129]

Arylchlorosilanes are also used in the synthesis of dichlorophosphines. The reaction takes place only in the presence of aluminium chloride, which cleaves the silicon–carbon bond under mild conditions with formation of the corresponding organoaluminium compounds. The latter react with phosphorus trichloride and afford aryldichlorophosphines in yields of 77–85%:[130,131,132]

$$(R_nC_6H_{5-n})_mSiCl_{4-m} + mAlCl_3 + mPCl_3 \rightarrow mR_nC_6H_{5-n}PCl_2 \cdot AlCl_3 ;$$
$$R = H, Cl, Br, C_1\text{–}C_4 \text{ alkyl}; \quad n = 0-5; m = 1-4 .$$

(c) Arylation of White Phosphorus by Aryl Halides

Aryl halides arylate white phosphorus at 250–450 °C in the presence of catalytic amounts of Lewis acids,[133–135] metal powders (Cu, Ag, and Zn),[136,137] or in the absence of a catalyst[138–140] with formation of a mixture of aryldihalogeno- and diarylhalogenophosphines, with the former predominating:

$$3R_nC_6H_{5-n}Hal + {}^1/_2P_4 \rightarrow R_nC_6H_{5-n}PHal_2 + (R_nC_6H_{5-n})_2PHal ;$$
$$R = H, Cl, CH_3; Hal = Cl, Br; n = 1, 2 .$$

When the reaction is carried out in phosphorus trihalide, the yield of aryldihalogenophosphines increases greatly, particularly in the presence of catalysts—sulphur, iodine, and halogeno-compounds. Thus dichlorophenylphosphine is obtained in 90% yield,[141–143] dibromo-2-tolylphosphine in 50.21% yield, and dichloro-4-fluorophenylphosphine in 73% yield.[144] Dichloro-2,4,5-trichlorophenylphosphine has been isolated in the form of a phosphonous acid in 57% yield.[145] The interaction of 1,4-dichlorobenzene with white phosphorus and PCl_3 leads to a mixture of 4-chlorophenyldichlorophosphine (I) and 1,4-bis(dichlorophosphino)benzene (II):

$$1,4\text{-}Cl_2C_6H_4 + {}^1/_2P_4 + 2PCl_3 \xrightarrow{I_2} \underset{(I)}{4\text{-}ClC_6H_4PCl_2} + \underset{(II)}{1,4\text{-}(Cl_2P)_2C_6H_4} .$$

The main reaction products are compound (I) at 290–300 °C and compound (II), in 38.4% yield, at 340 °C. Compound (I) is also converted into compound (II) on heating with white phosphorus and phosphorus dichloride, the yield being 24.7%.[146,147]

(d) Other Methods

Aryldichlorophosphines are obtained when complexes synthesised from arenediazonium fluoroborates and phosphorus trichloride are reduced with magnesium or aluminium:[148–155]

$$RC_6H_4\overset{+}{N}_2BF_4^- \xrightarrow{PCl_3} RC_6H_4\overset{+}{P}Cl_3BF_4^- \xrightarrow{M} RC_6H_4PCl_2 ;$$
$$R = 4\text{-}CH_3, 2\text{-}C_6H_5CH_2, 2\text{-}, 3\text{-} \text{ or } 4\text{-}Cl, 3\text{-}Br, 2\text{-}CH_3O, 2\text{-}(4\text{-}ClC_6H_4S), 3\text{-} \text{ or } 4\text{-}COOC_2H_5, 3\text{-} \text{ or } 4\text{-}CN; M = Mg, Al .$$

The reaction is exothermic, but can be readily controlled.

Arylhydrazines and their hydrochlorides give rise to aryldichlorophosphines in 45–65% yield on refluxing with phosphorus pentachloride in benzene:[156]

$$4\text{-}RC_6H_4NHNH_2 + PCl_5 \rightarrow 4\text{-}RC_6H_4PCl_2 + N_2 + 3HCl ;$$
$$R = CH_3, Cl, Br .$$

Dihalogenophenylphosphines are formed in 8.5–11.5% yields when a mixture of iodobenzene, phosphorus trihalide, and powdered silver is irradiated with UV light.[157]

Thus aryldichlorophosphines are usually obtained by the Friedel–Crafts reaction, which has in fact been more thoroughly investigated than other methods. The reaction is simple to carry out, the initial rectants are readily available, and the dichlorophosphines are obtained in satisfactory yields. Significant disadvantages of the method are the formation of a mixture of the 2-, 3-, and 4-isomers of aryldichlorophosphines, which are difficult to separate, a large amount of industrial waste,† and a limited selection of substituents in the aromatic ring.

3. Arylation of Phosphorus Trihalides by Arenediazonium Fluoroborates

A large number of different arylphosphonic acids have been synthesised by this method, although the first attempts to employ arenediazonium salts for the synthesis of arylphosphonic acids were unsuccessful.[23,110,158,159] Later arylphosphonic acids were synthesised by the reactions of fluoroborates with phosphorus trichloride in the presence of powdered copper bronze or univalent copper halides:

$$Ar\overset{+}{N}_2BF_4^- + PCl_3 \xrightarrow{Cu \text{ or } Cu_2Cl_2} Ar\overset{+}{P}Cl_3BF_4^- \xrightarrow{H_2O} ArPO_3H_2 .$$

The reaction is carried out in an anhydrous organic solvent, mainly ethyl and isopropyl acetate or dioxan, at room temperature of 50–60 °C. The reactants are taken in equimolar proportions. Phosphorus tribromide is rarely used.[160–164] Apart from arenediazonium fluoroborates, the diazonium chlorozincate and fluorosilicate salts are used. It has been noted that diazonium fluorosilicates are more stable and more convenient to handle.[164] The required compounds are isolated from concentrated aqueous solutions in the form of monosodium (monopotassium) salts of the free acids and are purified by recrystallisation, usually from 6 *N* HCl. The yields of arylphosphonic acids normally vary in the range 10–50% and rarely exceed 70%. Diarylphosphinic acids are formed as side products in yields up to 15%.

Phenylphosphonic acid is formed from benzenediazonium fluoroborate and phosphorus trichloride in 17% yield.[161] 3- and 4-Tolylphosphonic acids have been prepared in yields of 69.8 and 60% respectively[165] and all the isomers of ethylphenylphosphonic acid have been obtained in yields of 11–18%.[166] 4-(β-Bromoethyl)phenylphosphonic and

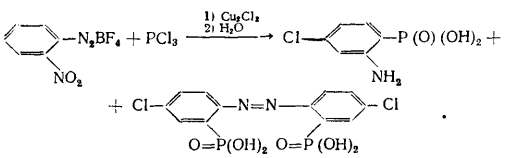
†Between 2.2 and 2.5 kg of solid waste and resins are obtained per kilogram of aryldichlorophosphine.[74]

4-(t-butyl)phenylphosphonic acids have been synthesised in yields of 36%[167] and 55%[39] respectively, while 2- and 4-biphenylylphosphonic acids have been obtained in yields of 9 and 40%.[168] (2,5-Diphenyl)phenylphosphonic acid is formed in 17% yield.[169]

Almost all the possible isomeric monohalogenophenylphosphonic acids, other than 3-bromo- and 4-iodo-substituted derivatives, have been synthesised in yields of 20–60%. They have been identified in a free state, with the exception of the 4-fluoro-derivative, which has been isolated in the form of the 4-toluidine salt. Iodobenzenediazonium salts react with phosphorus halides with greater difficulty and the yields of iodophenylphosphonic acids do not exceed 22%.[161,163,164,170–174]

When benzene-1,3- and benzene-1,4-disdiazonium fluoroborates are treated with phosphorus trichloride, only one diazo-group is phosphorylated, while the second is substituted by chlorine and partly by fluorine.[175] Di- and trihalogenobenzenediazonium fluoroborates react with phosphorus trichloride and tribromide under the same conditions to form di- and tri-halogenophenylphosphonic acids in yields up to 32%.[163,173] The isomeric 2-chloro-5-methyl-, 3-chloro-4-methyl-, and 4-chloro-3-methyl-phosphonic acids have also been obtained by this method in yields of 36, 50, and 15% respectively.[162,176]

3(4)-Nitrophenyl- and 4(5)-nitro-2(3)-tolyl-phosphonic acids are obtained by the diazo-method in yields of 37 to 55%.[161,164,174,177] 2-Nitrophenyl- and dinitrophenyl-phosphonic acids could not be obtained by this method.[161,170] The interaction of 2-nitrobenzenediazonium fluoroborate with phosphorus trichloride is accompanied not only by the substitution of the diazo-group by the dichlorophosphonyl group but also by the reduction of the nitro-group to the amino-group and by the chlorination of the aromatic ring. 2-Amino-4-chlorophenylphosphonic acid and 4,4′-dichloro-2,2′-diphosphonoazobenzene were isolated in low yields from the reaction mixture:[178]



The catalyst is used in an equivalent amount and the ArN_2BF_4 : PCl_3 ratio is 1 : 3.5. In the presence of a smaller excess of the phosphorus halide, the yield of the arylphosphonic acid is appreciably reduced. Chloroaminophenylphosphonic acid is isolated from its complex with a copper salt on treatment with hydrochloric acid in a yield up to 15%.[179–181] The phosphorylation of monohalogeno-derivatives of 2-nitrobenzenediazonium fluoroborates proceeds without the halogenation of the aromatic ring but with reduction of the nitro-group regardless of the position of the halogen atom.[182] The use of reductants, for example, of powdered iron in hydrochloric acid, makes it possible to raise the yield of 2-amino-4-halogenophenylphosphonic acids to 33%.[182] 2-Hydroxyphenylphosphonic acid cannot be synthesised by this method; only the products of its coupling with 4-nitrobenzenediazonium chloride were isolated from the reaction mixture in a small amount.[179,183]

Alkoxyphenyl-, benzyloxyphenyl-, 3,4-di(hydroxymethyl)-phenyl-, and alkylthiophenyl-phosphonic acids have been synthesised from the corresponding diazonium salts and phosphorus trichloride in yields of 18–61%[173,174,184,185] and 2-phenoxyphenylphosphonic acid has been obtained in 63% yield.[186]

Arylphosphonic acids containing the carbonyl, sulphonamido-, and cyano-substituents, which are difficult to obtain by other methods, can be synthesised by the diazo-method in yields of 27–50%.[161,173,187]

Thus 2-carboxyphenylphosphonic acid has been obtained from the diazonium salt of anthranilic acid and phosphorus trichloride in one stage in a yield of 37%; previously its synthesis involved several stages.[173] The corresponding arylphosphonic acids have been synthesised in yields of 12–44% by this procedure from arenediazonium salts containing several different functional groups in the ring—one or two halogen (F, Cl, Br) atoms and the nitro-group,[163,173,184,188] a chlorine atom and the hydroxy-group[183] or the methoxy-group,[186] and the nitro and methoxy- or carboxy-groups.[173,177] For example, 2-methoxy-4-nitrophenylphosphonic acid has been obtained in 31% yield and used to synthesise 4-amino-2-hydroxyphenylphosphonic acid—the phosphorus analogue of 4-amino-salicyclic acid.[173]

It follows from the foregoing that the diazotisation method is simple to carry out and makes it possible to obtain arylphosphonic acids with a wide range of substituents in the aromatic ring, which are either difficult to obtain or cannot be obtained at all by other procedures. The disadvantages of the method include a comparatively low yield of the required substances, which rarely exceeds 50%, and its unsuitability for the synthesis of 2-nitro- and 2-hydroxy-phenylphosphonic acids as well as a number of other substituted arylphosphonic acids.

4. Arylation of Phosphorus Pentoxide and Pentasulphide

Aromatic compounds with hydroxy-, amino-, nitro-, and other groups which can undergo any kind of changes under the conditions of the synthesis are used as arylating agents in this procedure. The reaction is carried out in an autoclave at 150–225 °C using phosphorus pentasulphide and at 250–325 °C with phosphorus pentoxide, the reaction time being 5–25 h. The aromatic compound is taken in a large excess. The reaction products are hydrolysed with water to arylphosphonic acids. Thus, when anisole and phosphorus pentasulphide were used, 4-methoxyphenylphosphonic acid was obtained in 80% yield:[189–195]

$$RC_6H_5 + P_4X_{10} \xrightarrow{1)\,\Delta\ 2)\,H_2O,\,\Delta} RC_6H_4P(O)(OH)_2\ ;$$

R=H, CH_3, Cl, OCH_3, OC_2H_5; X=O, S .

The reaction proceeds with the preliminary dissociation of one bond in the hexagonal form of the phosphorus pentachalcogenide and the formation of a biradical or a dipolar ion, which then reacts with the aromatic compound to form the polymeric anhydrides of arylphosphonic or arylphosphonothioic acids.[189] Treatment of the anhydrides, thioanhydrides, and mixed thioanhydrides of the arylphosphonic acids with sulphuryl chloride, phosphorus pentachloride, or chlorine and then with sulphur dioxide leads to the dichlorides of arylphosphonic acids.[189,194,196–198] The latter can also be obtained by heating the aryl halides 4-RC_6H_4Hal (R = H, C_1–C_4 alkyl or Cl and Hal = Cl, Br) directly with phosphorus pentoxide and phosphorus trihalide at 200–450 °C.[199]

When tetra-aryloxysilanes and triphenyl borate react with phosphorus pentasulphide, compounds (III) are formed and are then hydrolysed with water to hydroxyarylphosphonic acid in yields up to 40%:[200,201]

$$(RC_6H_4O)_nZ + P_4S_{10} \xrightarrow{170^\circ} \left\{\left[-S-\overset{\overset{S}{\|}}{P}(R)\,C_6H_3O\right]_n Z\right\}_2 \xrightarrow{H_2O,\,\Delta}$$

(III)

$$\rightarrow 4\text{-HO}(R)\,C_6H_3PO_3H_2\ ;$$

R=H, 3-CH_3; $n=3$, Z=B; $n=4$, Z=Si .

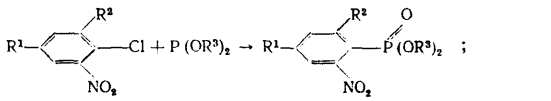
As a result of limitations in the choice of substituents in the benzene ring and preparative difficulties, the above procedure has not received extensive recognition.

5. Arylation of Phosphite Esters by Aryl Halides

This Section describes the methods of synthesis of neutral esters of arylphosphonic acids with different substituents in the ring by arylating the esters of phosphorous acids by aromatic halides or nitro-compounds.

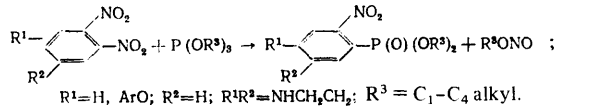
(a) Arylation without Initiators

4-Substituted tetrafluorophenylphosphonates have been obtained in 25–30% yields by the prolonged (16 h) heating (to 150 °C) in an autoclave of substituted pentafluorobenzenes (RC_6F_5, where R = H, CF_3, CN, NO_2, or C_6F_5) and triethyl phosphite.[202,203] When nitro-groups are present in the benzene ring in addition to the halogen atom, the reaction takes place at low temperatures (60–120 °C) with retention of the nitro-group and yields of the phosphonate up to 95%:[204–208]



R^1=H, CF_3, Cl, CN, NO_2, $C_2H_5SO_2$, CH_3COO; R^2=H, Cl, NO_2; R^3 = C_1–C_4 alkyl.

o-Dinitrobenzenes without a halogen arylate trialkyl phosphites in acetonitrile with formation of *o*-nitrophenylphosphonate in yields of 50–80%:[209–214]



R^1=H, ArO; R^2=H; R^1R^2=$NHCH_2CH_2$; R^3 = C_1–C_4 alkyl.

The nitro-group in 5(6)-nitrobenzimidazole is readily substituted by the phosphoryl group on heating with dialkyl phosphites.[215]

(b) Arylation in the Presence of Catalysts

Various arylphosphonates have been obtained in yields up to 90% by heating dialkyl phosphites[216–219] or trialkyl phosphites[220–234] with aryl halides in the presence of catalysts:

$$(R^1O)_2PONa + R^2Hal \xrightarrow{CuI} R^2P(O)(OR^1)_3 ;$$

R^1=C_2H_5, C_6H_5; R^2=C_6H_5, 4-$CH_3C_6H_4$, 4-$NH_2C_6H_4$, 2,4,6-$(CH_3)_3C_6H_2$, $(CH_3)_5C_6$; Hal=Br, I .

The best catalysts are nickel halides, used in an amount of 0.1–20 mole %,[220–225] and palladium chloride or acetate—0.01 0.01–0.05 mole %.[228,229] Copper bronze and copper(I) chloride give poorer results even when a threeefold excess of the phosphite is employed,[230,231] while alkylation in the presence of copper(I) iodide or copper acetate proceeds at comparatively low temperatures (0–115 °C) in a solvent, the yield of the phosphonates reaching 85%.[216,217,232–234] A complex of palladium halide with triphenylphosphine is also used as the catalyst.[218,219]

On heating to 250–340 °C in the presence of catalytic amounts of iodobenzene and nickel or copper halides, triphenyl phospite isomerises to diphenyl phenylphosphonate in yields up to 90%. In the presence of iron(III) chloride, less satisfactory results were obtained.[226]

The interaction of the sodium salts of dialkyl or diaryl phosphites with aryl halides takes place in the presence of copper(I) iodide or magnesium iodide. The yields of the arylphosphonates are 54–81%:[227,235]

$$R^1_nC_6H_{5-n}Hal + R^2OP(OR^3)_2 \rightarrow R^1_nC_6H_{5-n}P(O)(OR^3)_2 + R^2Hal ;$$

n=1, R^1=H, Cl, F, CH_3, $C_{12}H_{25}$, OH, OCH_3, OC_6H_5, SCH_3, $COCH_3$, $COOCH_3$, $COOC_2H_5$, $N(CH_3)_2$, CH_2NH_2, NO_2, CN; n = 3, R^1=H, CH_3, $(CH_3)_3C$, OH, NH_2, $HNCOCH_3$, $N(C_2H_5)_2$, $N{=}NC_6H_3(R^1)N(C_2H_5)_2$; R^2=H, R^3; R^3=CH_3, C_2H_5, *изо*-C_3H_7; R^1=H, CH_3, C_2H_5, NO_2; Hal=Cl, Br, I.

(c) Arylation under Ultraviolet Irradiation

When a mixture of an aryl halide with a three-fivefold excess of trimethyl or triethyl phosphite is irradiated for a long time, dialkyl arylphosphonates are formed in a satisfactory yield. The optimum reaction temperature ranges from −5° to −25 °C. Aryl iodides or bromides are best as arylating agents. The dimethyl esters of phenyl-, tolyl-, and xylyl-phosphonic acids are obtained in yields of 50 to 100%. When triethyl phosphite is arylated, a more prolonged irradiation is required than in the arylation of trimethyl phosphite; with increase of the length of the group R in the phosphites $(RO_3)P$, the yield of aryl phosphonates is sharply reduced. Thus when tri-isopropyl phosphite and iodobenzene are used, the yield of di-isopropyl phenylphosphonate is only 26%.[236–242]

The reaction of dihalogenobenzenes and trimethyl phosphite affords dimethylhalogenophenyl phosphonates, the best yields (39–92%) having been achieved using 1,3- and 1,4-isomers and a combination of halogens: I and Cl or Br; Br and F. The side products of the reaction are phenylenediphosphonates, whose yield depends on the nature and positions of the halogen atoms in the dihalogenobenzene, reaching 87% when 1,2-bromoiodobenzene is employed and 10–39% in the case of the 1,3- and 1,4-isomers.[239,240] Pentafluoro- and pentachloro-pyridines interact with the lowest phosphites to form tetrahalogenopyridylphosphonates.[241]

Various isomers of methoxy- and dimethoxy-phenylphosphonic acids,[238,242,243] hydroxyphenylphosphonic acid,[238,242] aminophenylphosphonic acid,[244] formylphenylphosphonic acid,[243] and ethoxycarbonylphenylphosphonic acid[245] have been obtained by the reaction of substituted iodobenzenes with lower trialkyl phosphites in 34–92% yields. This method proved to be unsuitable for the synthesis of nitrophenylphosphonates because of the occurrence of oxidation-reduction processes in the interaction of nitrobenzene with phosphites.[238]

The sodium or potassium salts of dialkyl phosphites and *NNN'N'*-tetra-alkylphosphorodiamidous acids interact with aryl bromides or, better, iodides in liquid ammonia on irradiation with UV light with formation of phosphonates in 87–96% yield. Without illumination, the yield of the required compound is very low (0–7%):[246–252]

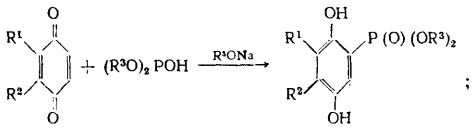
$$R^1_nC_6H_{5-n}Hal + MOPR^2_2 \rightarrow R^1_nC_6H_{5-n}P(O)R^2_2 ;$$

n=1, R^1=H, CH_3, CF_3, F, Cl, Br, I, OH, NH_2, $CONH_2$, OCH_3, $COOC_2H_5$; n=2, R^1=CH_3; R^2=OCH_3, OC_2H_5, $N(CH_3)_2$; Hal=Cl, Br; M=K, Na .

Under the same conditions, 1,3-dibromo- and 1,3-chloroiodobenzenes react with alkali metal salts of dialkyl phosphites, forming preferentially the tetra-alkyl esters of 1,3-phenylenebisphosphonic acids.[253,254] Instead of liquid ammonia, it is also possible to use other solvents (dimethyl sulphoxide, dimethyl formamide, t-butyl alcohol, and acetonitrile).[255]

6. Other Methods

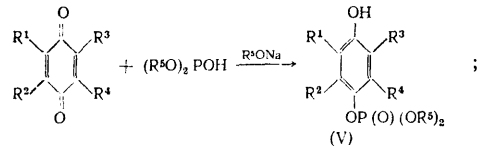
In the first communication[256] on the interaction of *p*-quinones with dialkyl phosphites in the presence of bases, it was suggested that the reaction product has the phosphonate structure (IV):



(IV)

$R^1=R^2=H$; $R^1R^2=(CH)_4$; $R^3 = C_1$-C_{20} alkyl.

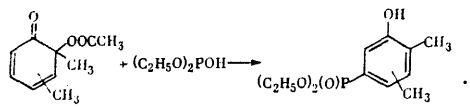
In subsequent studies[257–261] evidence was obtained showing that the product of this reaction is the phosphate (V):



(V)

$R^1=R^2=R^3=R^4=H$, Cl; $R^1=R^2=H$; $R^3R^4=(CH)_4$; $R^5=CH_3$, C_2H_5 .

The interaction of dimethyl phosphite with *p*-benzoquinone, which leads to the formation of a mixture of 55% of the phosphonate (IV, $R^1 = R^2 = H$, $R^3 = CH_3$), 10% of the phosphate (V, $R^1 = R^2 = R^3 = H$, $R^5 = CH_3$), and 8% of the bisphosphonate [IV, $R^1 = H$, $R^2 = P(O)(OCH_3)_2$] was later described.[262] The interaction of *p*-benzoquinone-bisbenzenesulphonyl imide with lower dialkyl phosphites also leads to a mixture of a phosphonate and a phosphoramidate whose ratio varies with the reaction conditions.[263] 3-Hydroxyarylphosphonates have been obtained in yields up to 40% by the reaction of substituted 2-acetoxy-2-methylcyclohexa-3,5-dienones with diethyl phosphite:[264]



In the study of the interaction of *p*-quinones with lower trialkyl phosphites, different workers also obtained contradictory data. Thus it has been claimed[265,266] that the products of this reaction are 2-alkoxy-5-hydroxyphenylphosphonates, in other investigations[267–269] the products were believed to be 4-alkoxyphenyl phosphates, while in yet another study[270] they were said to be 4-alkoxyphenyl phosphates with an admixture of 2,5-dihydroxyphenylphosphonate (up to 2%). The reaction of triethyl phosphite with benzoquinone and hydrogen chloride in ether at −70 °C leads to a 1:1 mixture of the phosphate and phosphonate.[271]

When aryl 4-bromophenyl sulphides or aryl 4-bromophenyl ethers are heated with equimolar amounts of phosphorus trichloride and aluminium chloride with subsequent alkaline hydrolysis, the phosphonic acids $ArXC_6H_4PO_3H_2$-4 are formed in 75–90% yields for X = O and 12.5–67% yields for X = S and Ar = $C_6H_4R^2$-4; $R^2 = CH_3$, F, Cl, or Br.[148,149]

The electrochemical oxidation of a mixture of trialkyl phosphite and an 18–25-fold excess of an aromatic hydrocarbon in acetonitrile at room temperature results in the formation of dialkyl arylphosphonates in 14–66% yields:[272–276]

$$(R^1O)_3P + R^2_nC_6H_{6-n} \rightarrow (R^1O)_2P(O)C_6H_{5-n}R^2_n \ ;$$

$R^1 = C_1$-C_3 alkyl; $R^2 = H$ or C_1-C_4 alkyl; $n = 1, 2$.

When benzene or chlorobenzene was heated with phosphorus trichloride and benzoyl peroxide, the dichlorides of phenyl- and chlorophenylphosphonic acids were obtained respectively.[277] The interaction of dialkyl phosphites with benzoyl peroxide leads to the formation of 4-carboxyphenyl phosphonates in 55% yield.[278,279] In the presence of t-butyl peroxide, dialkyl phosphites react with aromatic hydrocarbons. After the acid hydrolysis of the reaction products, aryl phosphoric acids are obtained in yields up to 65%:[280,281]

$$R^1C_6H_4R^2 + (R^3O)_2POH \xrightarrow[1,\Delta\ 2)\ HCl]{[(CH_3)_3CO]_2} R^1(R^2)C_6H_3P(O)(OH)_2 \ ;$$

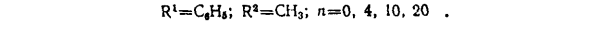
R^1=H, CH_3, CH_3O, Br, CH_3OOC; R^2=H, CH_3; $R^1R^2=(CH)_4$; $R^3=CH_3$, C_2H_5.

In the presence of strong bases, for example, lithium di-isopropylamide, dialkyl phenyl phosphate rearranges to 2-hydroxyphenylphosphonate in yields up to 98%.[282] The diethyl esters, ester-amides, and diamides of arylphosphonic acids, containing various substituents have been synthesised by the reaction of aryl-lithium or arylmagnesium halides with dialkyl phosphorochloridates in yields of 5.7–65.4%[225,243,289–293] and with phosphorodiamidic chlorides in yields of 18–75.2%.[290,291] 2,5-Dichlorophenyl (*N*-isopropyl)phenylphosphonamidate has been obtained in 26.6% yield.[292] The reaction is carried out in absolute ether or tetrahydrofuran:

$$R^1_2P(O)Cl + R^2_nC_6H_{5-n}M \rightarrow R^1_2P(O)C_6H_{5-n}R^2_n \ ;$$

R^1=CH_3O, C_2H_5O, NHC_6H_5, NC_5H_{10}; R^2=H, CH_3, CH_3O, Cl, Br, C_6H_5, $(CH_3)_3SiCH_2$, $(CH_3)_3Si$, $C_4H_9SCH_2$; $n = 1, 2$:
M=Li, MgCl, MgBr .

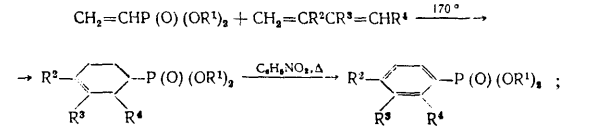
Bisphosphorylated siloxanes have been obtained in this way from diphenyl phosphorochloridate in siloxanes containing two phenylmagnesium bromide groups at different silicon atoms:[293,294]



$R^1=C_6H_5$; $R^2=CH_3$; n=0, 4, 10, 20 .

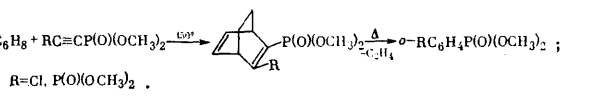
Tetraphenyl-lead or tetraphenyl–tin arylate phosphoryl chloride on prolonged (130–180 h) heating (to 180 °C) with formation of phenylphosphonic dichloride in yields up to 58%.[121,122]

The diene synthesis reaction is sometimes used to obtain the esters of arylphosphonic acids. Thus arylphosphonates have been obtained in yields up to 68% from diethyl vinylphosphonate and substituted butadienes with subsequent dehydrogenation of the reaction products.[295]



$R^1=C_2H_5$; R^2, R^3=H, CH_3; $R^4=R^2$, CH_3O .

2-Substituted dimethyl arylphosphonates are obtained from cyclohexadiene and dimethyl chloroethynylphosphonate or tetramethyl ethynylenediphosphonate. The reaction involves the formation of a bicyclic phosphonate which splits off ethylene at a high temperature and affords the aryl phosphonate:[296]



R=Cl, $P(O)(OCH_3)_2$.

2,5-Diphenylphenylphosphonic acid is obtained from maleic anhydride and 3-(2,5-diphenylfuryl)phenylphosphonic acid in 10–15% yield.[170] Dialkyl 5-acyl-2-isopropyl-4-methylphenylphosphonate has been obtained by heating dialkyl 3,3-dimethyl-1-vinylallenylphosphonate and acetylacetone in the presence of sodium ethoxide.[297]

III. METHODS OF SYNTHESIS OF ARYLPHOSPHONOTHIOIC ACIDS AND THEIR DERIVATIVES

Few methods are available for the synthesis of arylphosphonothioic acids and their derivatives and the choice of substituents in the aromatic ring (namely alkyl, alkoxy-, or halogeno-groups) is limited.

The dichlorides of arylphosphonothioic acids $R_nC_6H_{5-n}\cdot P(S)Cl_2$ ($R = C_1-C_{30}$ alkyl, F, Cl, Br, or CF_3 and $n = 1$ or 2) are obtained by adding sulphur to the aluminium chloride complex of an aryldichlorophosphine[95,298-300] or to free aryldihalogenophosphines in the presence of catalytic amounts of aluminium chloride[25,301] and ammonium or phosphonium salts.[302]

Successive treatment of dichlorophenyl- or chlorophenyldichlorophosphines with sulphur monochloride and sulphur dioxide or phosphorus pentoxide yields a mixture of the dichlorides of the corresponding arylphosphonic and arylphosphonothioic acids with the latter predominating.[303] On heating with thiophosphoryl chloride, 4-chlorophenyldichlorophosphine is converted into the dichloride of 4-chlorophenylphosphonothioic acid in 93.1% yield.[304] The esters, amides, and anhydrides of arylphosphonothioic acids are obtained by adding sulphur to the corresponding derivatives of arylphosphonous acids in yields up to 90%[5,34,43,104,304-306] or by oxidising the esters of arylphosphonothious acids with hydrogen peroxide.[305] The dihalides of arylphosphonothioic acids are obtained in yields of 10–79% on heating thiophosphoryl halide and an aromatic hydrocarbon with aluminium and aluminium chloride[307-311] or by heating an aromatic hydrocarbon with aluminium chloride, phosphorus trihalide, and phosphorus pentasulphide:[309,310,312-316]

$$RC_6H_5 + PSHal_3 \xrightarrow{AlCl_3,\ \Delta} RC_6H_4P(S)Hal_2\ ;$$
$$R=H,\ CH_3,\ F,\ Cl;\ Hal=Cl,\ Br\ .$$

When aluminium chloride is used, the $PSHal_3 : AlCl_3 : ArH$ reactant molar ratios are 1:2–2.5:1–1.1. The side products are the halides of diarylphosphinothioic acids and triarylphosphine sulphides, whose amount increases with increase of the reaction time as the reactant ratio is altered. Thus, after the reactant mixture had been refluxed for 4 h, the above two impurities were isolated in yields of 30 and 70% ($Ar = C_6H_{13}C_6H_4$).[315,316]

The phosphorylation of aromatic hydrocarbons by thiophosphoryl halides[317-320] or by a mixture of phosphorus trihalide and sulphur[321] as well as the phosphorylation of aryl halides by phosphorus sulphide (P_4S_3) [322] or mixtures of phosphorus sulphide (P_4S_{10}) with phosphorus trihalides[199,323] containing red phosphorus,[324] thiophosphoryl halides,[325] or thiophosphoryl halides and red phosphorus[326] as additives leads to the formation of the dihalides of arylphosphonothioic acids $RnC_6H_{5-n}P(S)Hal_2$ ($R = H$, C_1-C_4 alkyl, F, or Cl; $n = 1$ or 2; Hal = Cl or Br). The same products have been obtained by phosphorylating aryl halides with a mixture of thiophosphoryl halide with white or red phosphorus[327,328] or a mixture of phosphorus trihalide with phosphorus and sulphur.[329] The yield of the products is 35–87%. All these reactions take place at 200–450 °C. The reaction temperature falls following the addition of iodine, metal iodides, and alkyl iodides in an amount equivalent to 0.01–0.1% of the weights of the reaction mass.[323,327] The phosphorylation of toluene affords a mixture containing equal amounts of the dihalides of 4-tolylphosphonothioic and benzylphosphonothioic acids.[317-319]

The tetrachlorides of 1,4-arylenebis(phosphonothioic) acids are formed in 60–66% yield when 1,4-dichlorobenzene is heated with phosphorus trichloride and pentasulphide or with thiophosphoryl chloride and white phosphorus.[323,324,327,329]

The dihalides of arylphosphonothioic acids are obtained in 30–91.2% yields when an excess of phosphorus trihalide is heated with di- and tri-aryl phosphorothioites,[330-332] triaryl phosphorotetrathioates,[333] and diaryl sulphides[334,335] and disulphides[336] at 250–600 °C in the presence of catalytic amounts of halogens, halogeno-containing heterocarbons, metal halides, or without a catalyst. The halides of diarylphosphinothioic acids are formed as side products. For example:

$$(R_nC_6H_{5-n}S)_3P + PHal_3 \xrightarrow{\Delta} R_nC_6H_{5-n}P(S)Hal_2 + (R_nC_6H_{5-n})_2P(S)Hal\ ;$$
$$n=1,\ R=CH_3,\ (CH_3)_3C,\ C_9H_{19};\ n=2,\ R=Hal;\ Hal=Cl,\ Br\ ;$$

$$(R_nC_6H_{5-n})_2S + PHal_3 \xrightarrow{\Delta} R_nC_6H_{5-n}P(S)Hal_2 + (R_nC_6H^{5-n}{}_2)P(S)Hal\ ;$$
$$R=CH_3,\ C_2H_5;\ n=1-3;\ Hal=F,\ Cl,\ Br\ .$$

A mixture of phosphorus trihalide with white phosphorus[337,338] or with thiophosphoryl halide and phosphorus sulphides (of the type P_4S_n, where $n = 3$, 5, 7, or 10) has been introduced into the reaction with diaryl sulphides and disulphides.[339] The dichlorides of arylphosphonothioic acids are also formed in 65–90% yield when phosphorus trichloride is heated with arenethiols at 250–320 °C, but this requires the preliminary refluxing of the mixture of the initial reactants at atmospheric pressure:[340]

$$R_nC_6H_{5-n}SH + PCl_3 \rightarrow R_nC_nH_{5-n}P(S)Cl_2\ ;$$
$$R=H,\ Cl,\ (CH_3)_3C;\ n=1-5\ .$$

The thioanhydrides of arylphosphonothioic acids are obtained in 53.2–99% yield when a tenfold excess of *o*-xylene, anisole, and phenetole is heated with phosphorus pentasulphide[191,194,201,341,342] or with a mixture of phosphorus (white or red) and sulphur:[343-345]

$$R_nC_6H_{5-n} + P_4S_{10} \xrightarrow{150-170^\circ C} (R_nC_6H_{5-n}PS_2)_2\ ;$$
$$n=1,\ R=CH_3O,\ C_2H_5O;\ n=2,\ R=CH_3\ .$$

The dihalides of arylphosphonothioic acids are formed in 73–90% yield when the thioanhydrides of arylphosphonothioic and arylphosphonothious acids are treated with halogens and phosphorus pentachloride.[43,194,198]

On heating with thiophosphoryl halide, phosphorus pentasulphide,[346,347] white phosphorus, and sulphur,[348] the dihalides of arylphosphonic acids are converted into the dihalides of arylphosphonothioic acids.

The ester-halides of arylphosphonodithioic acids are formed when aryldihalogenophosphines react with sulphenyl chloride and hydrogen sulphide:[349,350]

$$ArPHal_2 \xrightarrow[2)\ H_2S]{1)\ ClSCH_2CH_2OR} ArP(S)(SCH_2CH_2OR)Hal\ .$$

They are also formed when the above compounds are heated with sulphenyl chloride in liquid sulphur dioxide or glacial acetic acid in the absence or presence of an inert solvent (methylene chloride or chloroform) at temperatures between −40° and 35 °C:[351-354]

$$R^1C_6H_4PCl_2 + R^2SCl \xrightarrow{CH_3COOH} R^1C_6H_4P(O)(SR^2)Cl\ ;$$
$$R^1=F,\ Cl;\ R^2 = \text{alkyl},\ CH_2CH=CH_2,\ CH_2C_6H_5,$$
$$CH_2CH_2OCH_3,\ CH_2CH_2OAr\ .$$

The ester-chlorides are usually not isolated but are converted into esters and ester-amides of arylphosphonothiolic and arylphosphonodithioic acids in 70–90% yield by reactions with alcohols, mercaptans, and amines. The simultaneous addition of dichlorophosphine and sulphenyl chloride to an excess of the alcohol in the solvent leads to *OS*-dialkyl (or alkyl aryl) arylphosphonothiolates in 66–99% yield:[144]

$$R^1C_6H_4PCl_2 + R^2SCl + R^3OH \xrightarrow{-40^\circ C} R^1C_6H_4P(O)(SR^2)(OR^3)\ ;$$
$$R^1=F,\ Cl;\ R^2 = C_1-C_5\ \text{alkyl},\ C_6H_5;\ R^3=CH_3,\ (CH_3)_2CH\ .$$

The diethyl esters of 2,3,5,6-tetrafluoroarylphosphonothioic acids are formed in 37–41% yield when pentafluorobenzene derivatives are heated with sodium diethyl phosphorothioite in tetrahydrofuran.[335]

REFERENCES

1. L.D.Freedman and G.O.Doak, Chem.Rev., 1957, **57**(3), 479.
2. P.C.Crofts, Quart.Rev., 1958, **12**, 347.
3. A.W.Frank, Chem.Rev., 1961, **61**(4), 389.
4. British Appl.2048883 (1980); Chem.Abs., 1980, **95**, 43346.
5. E.L.Gefter and I.A.Rogacheva, Zhur.Obshch.Khim., 1964, **34**, 88.
6. B.P.1520236 (1978); Chem.Abs., 1979, **80**, 138016.
7. Yu.I.Baranov, O.F.Filippov, S.L.Varshavskii, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, 1968, **182**, 337.
8. A.Michaelis and A.Schenk, Annalen, 1918, **260**, 1.
9. G.B.Arnold and C.S.Hamilton, J.Amer.Chem.Soc., 1941, **63**, 2637.
10. P.G.Chantrell, C.A.Pearce, C.R.Toyer, and R.Twaits, J.Appl.Chem.L, 1964, **14**, 563.
11. G.Ya.Legin, Zhur.Obshch.Khim., 1973, **43**, 2202.
12. N.K.Bliznyuk, G.S.Levskaya,and S.L.Varshavskii, USSR P.247298 (1969); Byul.Izobret., 1969(16), 17.
13. BRD P.954244 (1956); Chem.Abs., 1959, **53**, 11305.
14. B.P.783697 (1957); Chem.Abs., 1958, **52**, 8194.
15. G.Kh.Kamai, F.M.Kharrasova, R.B.Sultanova, and S.Yu.Tkukhvatulina, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., 1962, **5**, 759.
16. US P.2867646 (1959); Chem.Abs., 1959, **53**, 12237.
17. Japanese P.49389 (1980); Chem.Abs., 1980, **93**, 168409.
18. US P.4252740 (1981); cl.260–543.
19. E.A.Smirnov, Yu.M.Zinov'ev, and V.A.Petrukhin, Zhur.Obshch.Khim., 1968, **38**, 1551.
20. N.K.Bliznyuk, L.D.Protasova, R.S.Klopkova, and T.A.Klimova, USSR P.487083 (1975); Byul.Izobret., 1975(37), 87.
21. B.Buchner and L.Lockhart, J.Amer.Chem.Soc., 1951, **73**, 755.
22. P.Melchiker, Chem.Ber., 1898, **31**, 2915.
23. M.P.Viout, J.Recherches Centre natl.recherche sci.. (Paris), 1954(28), 15; Chem.Abs., 1956, **50**, 7077.
24. E.Cherbulier, G.Weber, and J.Rabinowits, Helv. Chim.Acta, 1962, **45**, 2665.
25. L.T.Yagupol'skii and Zh.M.Ivanova, Zhur.Obshch. Khim., 1960, **30**, 4026.
26. E.L.Gefter, Symposium, "Metody Polucheniya Khimicheskikh Reaktivov i Preparatov" (Methods of Synthesis of Chemical Reagents and Preparations), Izd.VNIIKhR i OChKhV, Moscow, 1969, No.18, p.99.
27. Yu.N.Mitrasov, E.E.Vladykov, and V.V.Kormachev, USSR P.1051096 (1983); Byul.Izobret., 1983(40), 96.
28. Yu.N.Mitrasov, E.E.Vladykov, and V.V.Kormachev, USSR P.1051097 (1983); Byul.Izobret., 1983(40), 96.
29. A.B.Davankov, M.I.Kabachnik, V.V.Korshak, Yu.A.Leikin, R.F.Okhovetsker, and E.N.Tsvetkov, Zhur.Obshch.Khim., 1967, **37**, 1605.
30. A.D.F.Toy, J.Amer.Chem.Soc., 1948, **70**, 186.
31. US P.2482810 (1949); Chem.Abs., 1950, **44**, 658.
32. A.V.Kazakova, O.E.Nasakin, and V.A.Kukhtin, Symposium, Fosfororganicheskie Soedineniya i Monomery" (Organophosphorus Compounds and Monomers), Cheboksary, 1977, Vol.3, p.19.
33. M.I.Kabachnik and E.N.Tsvetkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1961, 1896.
34. E.N.Tsvetkov, D.I.Lobanov, and M.I.Kabachnik, Zhur.Obshch.Khim., 1968, **38**, 2285.
35. I.S.Protopopov and M.Ya.Kraft, Zhur.Obshch.Khim., 1964, **34**, 1446.
36. G.M.Kosolapoff and F.Huber, J.Amer.Chem.Soc., 1947, **69**, 2020.
37. US P.2594454 (1952); Chem.Abs., 1953, 1179.
38. US P.2632018 (1953); Chem.Abs., 1954, **48**, 2097.
39. G.M.Kosolapoff, J.Amer.Chem.Soc., 1954, **76**, 3222.
40. G.M.Kosolapoff, J.Amer.Chem.Soc., 1952, **74**, 4119.
41. M.Jutisz, E.Scoffone, and P.Liosa, Bull.Soc.chim. France, 1959, 1551.
42. G.M.Kosolapoff, J.Amer.Chem.Soc., 1948, **70**, 3465.
43. L.I.Mizrakh and V.P.Evdakov, Zhur.Obshch.Khim., 1966, **36**, 469.
44. Japanese P.88943 (1976); Chem.Abs., 1976, **85**, 177615.
45. Japanese P.93751 (1977); Chem.Abs., 1978, **88**, 121375.
46. A.Michaelis, Chem.Ber., 1873, **6**, 601.
47. A.Michaelis, Chem.Ber., 1875, **8**, 1313.
48. A.Michaelis, Annalen, 1876, **181**, 265.
49. H.Kohler, Chem.Ber., 1880, **13**, 1623.
50. A.E.Arbuzov, Zhur.Russ.Fiz.-Khim.Obshch., 1910, **42**, 398.
51. W.Pope and C.S.Gibson, J.Chem.Soc., 1912, **101**, 735.
52. J.Linder, W.Wirth, and B.Zannerbauer, Monatsh. Chem., 1937, **70**, 1.
53. US P.3210418 (1965); Chem.Abs., 1966, **64**, 2128.
54. US P.3029282 (1962).
55. US P.3709932 (1973).
56. Belgian P.822737 (1975); Chem.Abs., 1976, **84**, 74432.
57. US P.3954859 (1976).
58. B.P.1469003 (1977); cl.C2P.
59. A.Michaelis, Chem.Ber., 1879, **12**, 1009.
60. G.Kamai, Zhur.Obshch.Khim., 1932, **2**, 524.
61. G.M.Kosolapoff, in "Friedel—Crafts and Related Reactions" (Edited by G.A.Olar), Wiley, New York, 1965, Vol.4, p.213.
62. A.W.Frank, J.Org.Chem., 1959, **24**, 966.
63. F.M.Kharrasova, G.M.Kamai, and R.B.Sultanova, USSR P.185908 (1966); Byul.Izobret., 1966(18), 39.
64. W.T.Dye, J.Amer.Chem.Soc., 1948, **70**, 2595.
65. E.L.Gefter, USSR P.107277 (1957); Byul.Izobret., 1957(6).
66. E.L.Gefter, Zhur.Obshch.Khim.. 1958, **28**, 1338.
67. Japanese P.17485 (1960); Chem.Abs., 1981, **55**, 19861.
68. V.V.Kormachev, T.V.Vasil'eva, A.I.Abramov, and A.Yu.Klubov, USSR P.1011653 (1983); Byul. Izobret., 1983(14), 101.
69. V.V.Kormachev, K.V.Solodova, T.N.Vorozhtseva, T.V.Vasil'eva, and S.P.Chalykh, Zhur.Obshch. Khim., 1984, **54**, 1004.
70. Japanese P.12054 (1975); Chem.Abs., 1975, **83**, 10393.
71. US P.2211707 (1940); Chem.Abs., 1941, **35**, 468.
72. W.C.Davies and F.G.Mann, J.Chem.Soc., 1944, p.276.
73. G.M.Kamai, F.M.Kharrasova, R.B.Sultanova, and G.I.Matveeva, Zhur.Obshch.Khim., 1967, **37**, 902.
74. R.K.Dybovskii and V.A.Rogozkin, Zhur.Prikl. Khim.. 1967, **40**, 228.

75. E.F.Gefter, in "Fosfororganicheskie Monomery i Polimery" (Organophosphorus Monomers and Polymers), Izd.Akad.Nauk SSSR, Moscow, 1960, p.98.
76. G.M.Kosolapoff, J.Amer.Chem.Soc., 1950, **72**, 4292.
77. B.Bucher and L.B.Lockhart, Org.Synt., 1951, **31**, 88.
78. F.G.Mann and E.J.Chaplin, J.Chem.Soc., 1937, **39**, 527.
79. F.Zecchini, Gazzetta, 1984, **24**, 34.
80. A.Michaelis, Annalen, 1896, **293**, 193.
81. R.A.Baldurn, K.A.Smitheman, and R.M.Washburn, J.Org.Chem., 1961, **26**, 3547.
82. R.H.Wiley and C.H.Jarboe, J.Amer.Chem.Soc., 1951, **73**, 4996.
83. J.Weller, Chem.Ber., 1887, **20**, 1718.
84. Europ.Appl.8164 (1980); Chem.Abs., 1980, **93**, 168404.
85. A.Michaelis, Annalen, 1901, **315**, 43.
86. BRD P.2152481 (1970); Chem.Abs., 1972, **77**, 62815.
87. BRD P.2215544 (1972); Chem.Abs., 1973, **78**, 85327.
88. T.V.Kovaleva, I.T.Rozhdestvenskaya, and N.G.Feshchenko, Zhur.Obshch.Khim., 1977, **47**, 318.
89. Europ.Appl.24128 (1981); Chem.Abs., 1981, **95**, 150884.
90. A.Michaelis, Annalen, 1897, **294**, 1.
91. W.C.Davies, J.Chem.Soc., 1935, **37**, 462.
92. G.A.Cook, J.Org.Chem., 1965, **30**, 1262.
93. V.V.Ponomarev, A.S.Shapatin, and S.A.Golubtsov, USSR P.184856 (1966); Byul.Izobret., 1966, **43**(16), 33.
94. V.V.Ponomarev, S.A.Golubtsov, K.A.Andrianov, and G.N.Kondrashov, Izv.Akad.Nauk SSSR, Ser. Khim., 1969, 1545.
95. H.Shindlbauer, Chem.Ber., 1967, **100**, 3432.
96. V.Gutman, E.Wychera, and E.Mairinger, Monatsh. Chem., 1966, **97**, 1265.
97. A.Hince and W.Kuchen, Phosphorus Sulfur, 1983, **15**, 93.
98. E.L.Gefter, Zhur.Obshch.Khim., 1962, **32**, 3401.
99. P.D.Bartlett and G.Meuerian, J.Amer.Chem.Soc., 1956, **78**, 3710.
100. K.G.Marathe, N.S.Limaye, and G.V.Bhide, J.Sci. Research, 1950, **98**(11), 268.
101. A.I.Bokanov and V.A.Plakhov, Zhur.Obshch.Khim., 1965, **35**, 350.
102. G.G.Yakobson, G.G.Furin, and T.V.Terent'eva, Zhur.Obshch.Khim., 1973, **9**, 1707.
103. I.S.Protopopov and M.Ya.Kraft, Med.Prom.SSSR, 1959(12), 5.
104. E.L.Gefter, Zhur.Obshch.Khim., 1963, **33**, 3548.
105. G.Kamai, Zhur.Obshch.Khim., 1934, **4**, 192.
106. G.Kamai, Trudy Kazan.Khim.-Tekhnol.Inst., 1934, **2**, 19.
107. J.A.Miles, M.T.Beeny, and K.W.Ratts, J.Org. Chem., 1975, **40**, 343.
108. US P.3974217 (1976); Chem.Abs., 1976, **86**, 177613.
109. M.P.Viout and P.Rumpf, Bull.Soc.chim.France, 1957, 768.
110. W.C.Davies and R.Morris, J.Chem.Soc., 1932, 2880.
111. V.S.Tsivunin, T.N.Lobanova, V.G.Zaripova, and T.V.Zykova, Zhur.Obshch.Khim., 1981, **51**, 1553.
112. V.V.Kormachev and I.A.Abramov, USSR P.551338 (1977); Byul.Izobret., 1977, **54**(11), 84.
113. M.Bourneuf, Bull.Soc.chim.France, 1923, **33**, 1808.
114. D.M.Coune, W.E.Ewen, and C.A.Werf, J.Amer. Chem.Soc., 1958, **78**, 3061.
115. G.P.Schiemenz, Chem.Ber., 1965, **98**, 65.
116. BRD Appl.3216380 (1983); Chem.Abs., 1984, **100**, 51836.
117. BRD Appl.3216381 (1983); Chem.Abs., 1984, **100**, 51838.
118. L.M.Yagupol'skii and P.A.Yufa, Zhur.Obshch.Khim., 1958, **28**, 2880.
119. Th.Weil, B.Prijs, and H.Erlenmeyer, Helv.Chim. Acta, 1952, **35**, 1412.
120. Th.Weil, B.Prijs, and H.Erlenmeyer, Helv.Chim. Acta, 1953, **36**, 1314.
121. US P.3321557 (1967); Chem.Abs., 1967, **67**, 73684.
122. L.Maier, J.Inorg.Nucl.Chem., 1962, **24**, 1073.
123. F.Challenger and L.R.Ridgway, J.Chem.Soc., 1922, **121**, 104.
124. F.Challenger and L.R.Ridgway, J.Chem.Soc., 1924, **125**, 864.
125. P.Koe and F.Bickelhaupt, Angew.Chem., Int.Ed., 1968, **6**, 567.
126. G.G.Furin, T.V.Terent'eva, A.I.Rezvukhin, and G.G.Yakobson, Zhur.Obshch.Khim., 1975, **45**, 1473.
127. M.Fild, O.Glemser, and J.Hollenberg, Z.Naturforsch., 1966, **21**, 920.
128. M.G.Barlow, M.Green, R.N.Haszeldine, and H.G.Higson, J.Chem.Soc.C, 1966, 1592.
129. BRD Appl.3134834 (1981); Chem.Abs., 1983, **99**, 22693.
130. A.Ya.Yakubovich and G.V.Motsarev, Dokl.Akad. Nauk SSSR, 1953, **88**, 87.
131. A.Ya.Yakubovich and G.V.Motsarev, Zhur.Obshch. Khim., 1953, **23**, 771.
132. A.Ya.Yakubovich and G.V.Motsarev, Zhur.Obshch. Khim., 1953, **23**, 1547.
133. US P.3557204 (1971); Chem.Abs., 1971, **75**, 6088.
134. US P.3651147 (1972).
135. K.G.Weinbery, J.Org.Chem., 1975, **40**, 3586.
136. BRD Appl.1122522 (1962); Chem.Abs., 1962, **57**, 16660.
137. L.Maier, Helv.Chim.Acta, 1962, **46**, 2026.
138. K.A.Petrov, V.V.Smirnov, A.Kh.Tsareva, and V.I.Emel'yanov, USSR P.130512 (1960); Byul. Izobret., 1960(15), 26.
139. K.A.Petrov, V.V.Smirnov, and V.I.Emel'yanov, Zhur.Obshch.Khim., 1961, **31**, 3027.
140. US P.3864394 (1975); Chem.Abs., 1975, **82**, 140301.
141. B.P.1465305 (1977); Cl.C2P.
142. N.K.Bliznyuk, Z.N.Kvasha, and A.F.Kolomiets, USSR P.179316 (1966); Byul.Izobret., 1966(5), 23.
143. N.K.Bliznyuk, Z.N.Kvasha, and A.F.Kolomiets, Zhur.Obshch.Khim., 1967, **37**, 890.
144. N.K.Bliznyuk, Z.N.Kvasha, and G.A.Madzhara, USSR P.406839 (1973); Byul.Izobret., 1973(46), 70.
145. N.K.Bliznyuk, S.P.Khokhlov, L.I.Markova, and S.L.Varshavskii, USSR P.247950 (1969); Byul. Izobret.. 1969(23), 13.
146. S.L.Varshavskii, Yu.I.Baranov, O.F.Filippov, M.I.Kabachnik, and N.K.Bliznyuk, USSR P.209455 (1968); Byul.Izobret., 1968, **45**(5), 31.
147. T.V.Kovaleva, I.T.Rozhdestvenskaya, and N.G.Feshchenko, Zhur.Obshch.Khim., 1979, **49**, 1228.
148. I.Granoth and A.Kalir, Chem.Comm., 1969, **6**, 260.
149. I.Granoth, A.Kalir, Z.Pelan, and E.D.Bergman, Isr.J.Chem., 1970, **8**, 613.
150. L.D.Quin and J.S.Humphrey, J.Amer.Chem.Soc., 1960, **82**, 3795.
151. L.D.Quin and R.E.Montgomery, J.Org.Chem., 1963, **28**, 3315.

152. L.D.Quin and J.S.Humphrey, J.Amer.Chem.Soc., 1961, **83**, 4124.
153. D.I.Lobanov, E.N.Tsvetkov, and M.I.Kabachnik, Zhur.Obshch.Khim., 1969, **39**, 841.
154. E.N.Tsvetkov, D.I.Lobanov, and M.I.Kabachnik, Teor.Eksper.Khim., 1966, **2**, 458.
155. I.G.Malakhova, E.N.Tsvetkov, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 2602.
156. A.M.Pinchuk, T.V.Khimchenko, and A.V.Kirsanov, USSR P.391148 (1973); Byul.Izobret., 1973(31), 74.
157. R.A.Bowie and O.C.Musgrave, J.Chem.Soc.C, 1966, 566.
158. D.R.Nijk, Rec.Trav.chim., 1922, **41**, 461.
159. V.M.Plets, Zhur.Obshch.Khim., 1937, **7**, 270.
160. US P.2653160 (1953); Chem.Abs., 1954, **48**, 10764.
161. G.O.Doak and L.D.Freedman, J.Amer.Chem.Soc., 1951, **73**, 5658.
162. L.D.Freedman and G.O.Doak, J.Org.Chem., 1959, **24**, 638.
163. J.M.Denham and R.K.Ingham, J.Org.Chem., 1958, **23**, 1298.
164. L.D.Freedman and G.O.Doak, J.Amer.Chem.Soc., 1953, **75**, 4905.
165. E.C.Ashby and G.M.Kosolapoff, J.Amer.Chem.Soc., 1953, **75**, 4903.
166. L.D.Freedman and G.O.Doak, J.Amer.Chem.Soc., 1955, **77**, 173.
167. R.H.Wiley and W.A.Trinder, J.Polym.Sci., 1960, **42**(139), 113.
168. H.H.Jaffé, L.D.Freedman, and G.O.Doak, J.Amer. Chem.Soc., 1954, **76**, 1548.
169. C.E.Griffin and J.T.Brown, J.Org.Chem., 1961, **26**, 853.
170. G.O.Doak and L.D.Freedman, J.Amer.Chem.Soc., 1953, **75**, 683.
171. G.O.Doak and L.D.Freedman, J.Amer.Chem.Soc., 1952, **74**, 753.
172. G.M.Kosolapoff and G.G.Priest, J.Amer.Chem.Soc., 1953, **75**, 4847.
173. L.D.Freedman, H.Tauber, G.O.Doak, and J.Magnuson, J.Amer.Chem.Soc., 1953, **75**, 1379.
174. R.W.Bost, L.D.Quin, and A.Roc, J.Org.Chem., 1953, **18**, 362.
175. G.M.Kosolapoff and J.J.Duncan, J.Amer.Chem. Soc., 1955, **77**, 2419.
176. L.D.Freedman and G.O.Doak, J.Org.Chem., 1965, **30**, 1263.
177. L.D.Freedman and G.O.Doak, J.Org.Chem., 1961, **26**, 2082.
178. A.M.Lukin and I.D.Kalinina, Dokl.Akad.Nauk SSSR, 1961, **137**, 873.
179. A.M.Lukin and I.D.Kalinina, Khim.Nauka i Prom., 1957(2), 400.
180. A.M.Lukin, I.D.Kalinina, and G.B.Zavarikhina, USSR P.134697 (1961); Byul.Izobret., 1961(1), 15.
181. A.M.Lukin, I.D.Kalinina, and G.B.Zavarikhina, Zhur.Obshch.Khim., 1960, **30**, 4072.
182. A.M.Lukin, G.B.Zavarikhina, and N.A.Bolotina, USSR P.165168 (1964); Byul.Izobret., 1964(18), 14.
183. A.M.Lukin and I.D.Kalinina, Zhur.Obshch.Khim., 1960, **30**, 1597.
184. V.L.Bell and G.M.Kosolapoff, J.Amer.Chem.Soc., 1953, **75**, 4901.
185. L.D.Freedman, G.O.Doak, and E.L.Petit, J.Org. Chem., 1960, **25**, 140.
186. L.D.Freedman and G.O.Doak, J.Org.Chem., 1958, **23**, 769.
187. G.O.Doak and L.D.Freedman, J.Amer.Chem.Soc., 1959, **81**, 3021.
188. US P.3442938 (1969); Chem.Abs., 1969, **71**, 39160.
189. H.Z.Lecher, T.H.Chao, K.C.Whitehouse, and R.A.Greenwood, J.Amer.Chem.Soc., 1954, **76**, 1045.
190. US P.2717906 (1955); Chem.Abs., 1956, **50**, 6508.
191. US P.2847458 (1958); Chem.Abs., 1959, **53**, 3178.
192. BRD P.963425 (1957); Chem.Abs., 1960, **54**, 8729.
193. BRD Appl.1009628 (1957); Chem.Abs., 1960, **54**, 1473.
194. H.Z.Lecher, R.A.Greenwood, K.C.Whitehouse, and T.H.Chao, J.Amer.Chem.Soc., 1956, **78**, 5018.
195. H.Z.Lecher, T.H.Chao, K.C.Whitehouse, and R.A.Greenwood, J.Amer.Chem.Soc., 1954, **76**, 1045.
196. US P.2814645 (1957); Chem.Abs., 1957, **52**, 5464.
197. B.P.763992 (1956); Chem.Abs., 1957, **51**, 15570.
198. US P.2870204 (1959); Chem.Abs., 1959, **53**, 11306.
199. US P.3897491 (1975).
200. V.K.Kushov and G.F.Bebikh, Dokl.Akad.Nauk SSSR, SSSR, 1961, **136**, 354.
201. G.F.Bebikh, Yu.A.Pentin, and T.V.Ershova, Zhur.Obshch.Khim., 1963, **33**, 3544.
202. L.N.Markovskii, G.G.Furin, Yu.G.Shermalovich, and G.G.Yakobson, Izv.Akad.Nauk SSSR, Ser. Khim., 1977, 2839.
203. L.N.Markovskii, G.G.Furin, Yu.G.Shermalovich, and G.G.Yakobson, Zhur.Obshch.Khim., 1979, **49**, 531.
204. Yu.G.Gololobov, P.P.Onis'ko, and V.P.Prokopenko, Dokl.Akad.Nauk SSSR, 1977, **237**, 105.
205. V.A.Bondar', V.M.Sidorenko, and V.V.Malovik, Zhur.Obshch.Khim., 1977, **47**, 953.
206. BRD Appl.2421070 (1975); Chem.Abs., 1976, **84**, 74430.
207. P.P.Onis'ko, T.I.Cherepenko, V.S.Petrenko, and Yu.G.Gololobov, USSR P.606317 (1980); Byul. Izobret., 1980(44), 296.
208. BRD Appl.2829710 (1980); Chem.Abs., 1980, **93**, 132619.
209. J.I.Cadogan, D.J.Scars, and D.M.Smith, Chem. Comm., 1966, **15**, 491.
210. J.I.Cadogan, Quart.Rev., 1968, **22**, 222.
211. J.I.Cadogan, D.J.Sears, and D.M.Smith, J.Chem. Soc.C, 1969, **10**, 1314.
212. Europ.Appl.14684 (1980); Chem.Abs., 1981, **94**, 103558.
213. P.A.Gurevich, P.A.Stepanov, T.V.Znakova, and A.I.Razumov, Zhur.Obshch.Khim., 1983, **53**, 2395.
214. Europ.Appl.71572 (1983); Chem.Abs., 1983, **99**, 38638.
215. G.L.Matevosyan, S.A.Volovatova, and P.M.Zavlin, Zhur.Obshch.Khim., 1980, **50**, 2803.
216. BRD Appl.2717091 (1977); Chem.Abs., 1978, **88**, 74456.
217. H.Hall and R.Price, J.Chem.Soc., Perkin Trans.I, 1979, 2873.
218. T.Hirao, T.Masunaga, V.Oshiro, and T.Agawa, Synthesis, 1981, p.56.
219. T.Hirao, T.Masunaga, N.Vamada, V.Oshiro, and T.Agawa, Bull.Chem.Soc.Japan, 1982, **55**, 909.
220. P.Tavs, Chem.Ber., 1970, **103**, 2428.
221. B.P.1200273 (1970).
222. US P.3493639 (1970); Chem.Abs., 1970, **72**, 90635.
223. Swiss P.505152 (1971).
224. Belgian P.725475 (1972).
225. R.C.Grabiak, J.A.Miles, and G.M.Schwenzer, Phosphorus Sulfur, 1980, **9**, 197.

226. US P.4113807 (1978); Chem.Abs., 1979, **90**, 5404.
227. A.Osuka, N.Ohmasa, Y.Hoshida, and H.Suzuki, Synthesis, 1983, p.69.
228. US P.3705214 (1972).
229. Japanese P.48994 (1982); Chem.Abs., 1982, **97**, 145012.
230. P.Tavs and F.Korte, Tetrahedron, 1967, **23**, 4677.
231. V.P.Kukhar and E.I.Sagina, Zhur.Obshch.Khim., 1977, **47**, 1662.
232. H.Hall and R.Price, J.Chem.Soc., Perkin Trans.I, 1979, 2634.
233. B.P.1521353 (1978).
234. J.A.Connor, A.C.Jones, and R.Price, Chem.Comm., 1980, 137.
235. C.E.Griffin and N.T.Castellucei, J.Org.Chem., 1961, **26**, 629.
236. J.B.Plumb, R.Obrycki, and C.E.Griffin, J.Org. Chem., 1966, **31**, 2455.
237. C.E.Griffin, R.B.Davison, and M.Gordon, Tetrahedron, 1966, **22**, 560.
238. R.Obrycki and C.E.Griffin, J.Org.Chem., 1968, **33**, 632.
239. R.Obrycki and C.E.Griffin, Tetrahedron Letters, 1966, 5049.
240. E.P.Kuba, S.T.Lin, and R.L.Harris, Organometallics, 1983, **2**, 1877.
241. W.Boerigk and G.Haegele, Chem.Ber., 1983, **116**, 2418.
242. J.B.Plumb and C.E.Griffin, J.Org.Chem., 1962, **27**, 4711.
243. D.W.Allen, B.G.Huntly, and M.T.Mellor, J.Chem. Soc., Perkin Trans.II, 1977, 789.
244. R.A.Naylor and A.Williams, J.Chem.Soc., Perkin Trans.II, 1976, 1908.
245. M.Gordon, V.A.Notaro, and C.E.Griffin, J.Amer. Chem.Soc., 1964, **86**, 1898.
246. J.F.Bunnett and R.H.Weiss, Org.Synth., 1978, **58**, 134.
247. J.F.Bunnett and X.Creay, J.Org.Chem., 1974, **39**, 3612.
248. S.Hoz and J.F.Bunnett, J.Amer.Chem.Soc., 1977, **99**, 4690.
249. J.F.Bunnett and R.P.Traber, J.Org.Chem., 1978, **43**, 1867.
250. K.Issleib and R.Vollmer, Z.Chem., 1978, **18**, 451.
251. J.E.Swartz and J.F.Bunnett, J.Org.Chem., 1979, **44**, 4673.
252. R.R.Bard, J.F.Bunnett, and R.P.Traber, J.Org. Chem., 1979, **44**, 4918.
253. J.F.Bunnett and S.J.Shafer, J.Org.Chem., 1978, **43**, 1873.
254. J.F.Bunnett and S.J.Shafter, J.Org.Chem., 1978, **43**, 1877.
255. J.F.Bunnett, R.G.Scamehorn, and R.P.Traber, J.Org.Chem., 1976, **41**, 3677.
256. US P.2553417 (1951); Chem.Abs., 1951, **45**, 6865.
257. B.A.Arbuzov, N.A.Polezhaeva, and V.S.Vinogradov, Izv.Akad.Nauk SSSR, Ser.Khim., 1960, 1219.
258. E.S.Shepeleva and P.I.Sanin, Symposium, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy II Konferentsii" (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of II Conference), Izd.Akad.Nauk SSSR, Moscow, 1962, p.207.
259. M.G.Voronkov and B.I.Ionin, Symposium, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy II Konferentsii" (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of II Conference), Izd.Akad.Nauk SSSR, Moscow, 1962, p.203.
260. M.M.Sidky and W.M.Adbou, Egypt.J.Chem., 1982, **25**, 397.
261. A.A.Kutyrev and V.V.Moskva, Zhur.Obshch.Khim., 1983, **53**, 2398.
262. E.K.Trutneva and Ya.A.Levin, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1684.
263. M.M.Sidky, M.R.Mahran, and M.F.Zayed, Phosphorus Sulfur, 1981, **9**, 337.
264. E.Fulmek, A.Siegel, F.Wessely, and H.Clodi, Monatsh.Chem., 1961, **91**, 1167.
265. V.A.Kukhtin and K.M.Orekhova, Dokl.Akad.Nauk SSSR, 1959, **124**, 819.
266. V.A.Kukhtin and K.M.Orekhova, Symposium, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy II Konferentsii" (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of II Conference), Izd.Akad.Nauk SSSR, Moscow, 1962, p.88.
267. F.Ramirez and S.Dershowitz, J.Org.Chem., 1958, **23**, 778.
268. I.V.Konovalova and A.N.Pudovik, Uspekhi Khim., 1972, **41**, 799 [Russ.Chem.Rev., 1972(5)].
269. F.Ramirez and S.Dershowitz, J.Amer.Chem.Soc., 1959, **81**, 587.
270. F.Ramirez, E.H.Chen, and S.Dershowitz, J.Amer. Chem.Soc., 1959, **81**, 4338.
271. T.Kh.Gazizov, A.M.Kibardin, and A.N.Pudovik, Zhur.Obshch.Khim., 1977, **47**, 1914.
272. Yu.M.Kargin, E.V.Nikitina, O.V.Parakin, G.V.Romanov, and A.N.Pudovik, Dokl.Akad. Nauk SSSR, 1978, **242**, 1108.
273. E.V.Nikitin, Yu.M.Kargin, O.V.Parakin, A.N.Pudovik, and G.V.Romanov, USSR P.655702 (1979); Byul.Izobret., 1979(13), 91.
274. H.Ohmori, S.Nakai, and M.Masui, J.Chem.Soc., Perkin Trans.I, 1979, 2023.
275. E.V.Nikitin, Yu.M.Kargin, A.S.Romakhin, O.V.Parakin, A.N.Pudovik, and G.V.Romanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2170.
276. E.V.Nikitin, A.S.Romakhin, O.V.Parakin, and A.V.Pudovik, Dokl.Akad.Nauk SSSR, 1982, **266**, 402.
277. M.Karelsky and K.H.Pausacher, Austral.J.Chem., 1958, **11**, 336.
278. US P.3178469 (1965); Chem.Abs., 1965, **63**, 634.
279. A.K.Brel', O.S.Bogdanova, A.Rakhimov, and F.V.Mudrii, USSR P.757539; Byul.Izobret., 1980(31), 93.
280. E.K.Fields and R.J.Rolin, Chem.Ind., 1960, **31**, 999.
281. US P.3054821 (1962); Chem.Abs., 1963, **58**, 4599.
282. L.S.Melvin, Tetrahedron Letters, 1981, **22**, 3375.
283. A.Burger and N.D.Dawson, J.Org.Chem., 1951, **16**, 1250.
284. N.D.Dawson and A.Burger, J.Org.Chem., 1953, **18**, 207.
285. K.A.Petrov, V.A.Chauzov, L.P.Chernobrovkina, and N.N.Baranov, Zhur.Obshch.Khim., 1975, **45**, 2428.
286. R.W.Bott, B.F.Dowden, and C.Eaborn, J.Organometal.Chem., 1965, **4**, 291.
287. R.W.Bott, B.F.Dowden, and C.Eaborn, J.Chem. Soc., 1965, 4994.
288. R.W.Bott, B.F.Dowden, and C.Eaborn, "International Symposium on Organometallic Chemistry. Sci.Comm.", Prague, 1965, p.290.

289. V.A.Kukhtin, A.P.Rakov, G.F.Rudnitskaya, V.N.Mishagin, and L.I.Zubtsova, Zhur.Obshch. Khim., 1975, **45**, 945.
290. D.C.Morisson, J.Amer.Chem.Soc., 1951, **73**, 5896.
291. B.M.Mikhailov and N.F.Kucherova, Dokl.Akad.Nauk SSSR, 1951, **78**, 5896.
292. A.F.Grapov, N.V.Lebedeva, and N.N.Mel'nikov, Zhur.Obshch.Khim., 1968, **38**, 2260.
293. US P.2889349 (1959); Chem.Abs., 1960, **54**, 418.
294. B.P.815231 (1959); Chem.Abs., 1960, **54**, 7134.
295. W.M.Daniewski and C.E.Griffin, J.Org.Chem., 1966, **31**, 3237.
296. D.Seyferth and J.D.H.Paetsch, J.Org.Chem., 1969, **34**, 1483.
297. Yu.M.Dazhgyan, G.A.Ponosyan, M.G.Voskanyan, and Sh.O.Badanyan, Zhur.Obshch.Khim., 1983, **53**, 930.
298. US P.2662917 (1953); Chem.Abs., 1954, **48**, 13711.
299. US P.3294745 (1966); Chem.Abs., 1967, **66**, 56695.
300. Japanese P.2925 (1960); Chem.Abs., 1960, **54**, 24551.
301. B.P.713412 (1954).
302. Europ.Appl.71783 (1983); Chem.Abs., 1983, **99**, 53965.
303. DDR P.11241 (1956); Chem.Abs., 1958, **53**, 6156.
304. E.N.Tsvetkov, D.I.Lobanov, and M.I.Kabachnik, Zhur.Obshch.Khim., 1968, **38**, 2285.
305. Belgian P.608802 (1962); Chem.Abs., 1962, **57**, 7311.
306. E.L.Gefter and I.A.Rogacheva, Zhur.Obshch. Khim., 1962, **32**, 3962.
307. DDR P.10881 (1955); Chem.Abs., 1958, **53**, 6518.
308. BRD P.1238024 (1967); Chem.Abs., 1967, **67**, 90934.
309. US P.3988368 (1976); Chem.Abs., 1977, **86**, 55777.
310. B.P.1458162 (1976); Cl.C2P.
311. Japanese P.138654 (1976); Chem.Abs., 1977, **86**, 140249.
312. Japanese P.138656 (1976); Chem.Abs., 1977, **86**, 140247.
313. Japanese P.138655 (1976); Chem.Abs., 1977, **86**, 140248.
314. Japanese P.138657 (1976); Chem.Abs., 1977, **86**, 140250.
315. L.Maier, Helv.Chim.Acta, 1964, **47**, 120.
316. US P.3504025 (1970); Chem.Abs., 1967, **67**, 90934.
317. Yu.G.Ukhing and A.D.Toi, USSR P.625615 (1978); Byul.Izobret., 1978(35), 173.
318. US P.3790629 (1974).
319. B.P.1362357 (1974); Chem.Abs., 1973, **79**, 137276.
320. BRD P.2803689 (1978); Chem.Abs., 1978, **89**, 197716.
321. US P.4133830 (1979).
322. US P.4076746 (1978); Chem.Abs., 1978, **89**, 43771.
323. P.S.Khokhlov, N.K.Bliznyuk, L.I.Markova, L.M.Solntseva, G.S.Levskaya, Z.N.Kvasha, L.D.Protasova, E.N.Matyukhina, S.L.Varshavskii, Yu.I.Baranov, B.Ya.Libman, and S.G.Zhemchuzhina, USSR P.284984 (1974); Byul.Izobret., 1974(31), 179.
324. N.K.Bliznyuk, P.S.Khokhlov, Z.N.Kvasha, L.I.Markova, G.S.Levskaya, L.D.Protasova, L.M.Solntseva, E.N.Matyukhina, S.L.Varshavskii, Yu.I.Baranov, B.Ya.Libman, and S.G.Zhemchuzhina, USSR P.653262 (1979); Byul.Izobret., 1979(11), 85.
325. US P.3968156 (1976).
326. US P.3803226 (1974).
327. N.K.Bliznyuk, P.S.Khokhlov, and Z.N.Kvasha, USSR P.332094 (1972); Byul.Izobret., 1972(10), 93.
328. US P.3726918 (1973).
329. N.K.Bliznyuk, P.S.Khokhlov, and Z.N.Kvasha, USSR P.332095 (1972); Byul.Izobret., 1972(10), 94.
330. N.K.Bliznyuk, Z.N.Kvasha, S.L.Varshavskii, Yu.I.Baranov, B.Ya.Libman, R.V.Strelt'tsov, L.D.Protasova, L.I.Markova, P.S.Khokhlov, G.A.Madzhara, and L.E.Kirilina, USSR P.337384 (1972); Byul.Izobret., 1972(15), 79.
331. US P.3457306 (1969); Chem.Abs., 1969, **71**, 91648.
332. US P.3457308 (1969); Chem.Abs., 1969, **71**, 91646.
333. US P.3962323 (1976).
334. US P.3457305 (1969); Chem.Abs., 1969, **71**, 81527.
335. US P.3457307 (1969); Chem.Abs., 1969, **71**, 124665.
336. US P.3429916 (1969); Chem.Abs., 1969, **70**, 106648.
337. US P.4000190 (1976).
338. N.K.Bliznyuk, Z.N.Kvasha, S.L.Varshavskii, Yu.I.Baranov, and B.Ya.Libman, USSR P.300472 (1971); Byul.Izobret., 1971(13), 97.
339. US P.4130583 (1971); Chem.Abs., 1979, **90**, 152352.
340. N.K.Bliznyuk, Z.N.Kvasha, G.A.Madzhara, and L.I.Markova, USSR P.298593 (1971); Byul.Izobret., 1971(11), 88.
341. US P.2954379 (1960); Chem.Abs., 1961, **55**, 4030.
342. G.F.Bebikh, E.F.Ponizovtsev, I.O.Zolotukhin, L.G.Angert, G.N.Mikhailova, G.I.Rutman, F.B.Gershanov, and V.A.Kalashnikov, USSR P.759524 (1980); Byul.Izobret., 1980(32), 104.
343. N.K.Bliznyuk and Z.N.Kvasha, USSR P.306132 (1971); Byul.Izobret., 1971(19), 86.
344. F.N.Mazitova and V.K.Khairullin, Zhur.Obshch. Khim., 1981, **51**, 958.
345. F.N.Mazitova and V.K.Khairullin, Zhur.Obshch. Khim., 1981, **51**, 558.
346. US P.2993929 (1961); Chem.Abs., 1962, **56**, 505.
347. O.N.Grishina and L.M.Bezzubova, Izv.Akad.Nauk SSSR, Ser.Khim., 1965, 1619.
348. N.K.Bliznyuk, A.F.Kolomiets, and P.S.Khokhlov, USSR P.172742 (1965); Byul.Izobret., 1965(14), 16.
349. BRD P.2652922 (1978); Chem.Abs., 1978, **89**, 109955.
350. US P.3489825 (1970); Chem.Abs., 1970, **71**, 67091.
351. A.A.Neimysheva, V.I.Savchuk, and L.I.Knunyants, Zhur.Obshch.Khim., 1966, **36**, 500.
352. B.M.Gladshtein and L.N.Shitov, USSR P.215973 (1968); Byul.Izobret., 1968(14), 26.
353. N.K.Bliznyuk, Z.N.Kvasha, and L.M.Solntseva, USSR P.390099 (1973); Byul.Izobret., 1973(30), 79.
354. Z.N.Kvasha, L.M.Solntseva, and N.K.Bliznyuk, USSR P.450814 (1974); Byul.Izobret., 1974(43), 60.
355. L.N.Markovskii, G.G.Furin, Yu.G.Shermolovich, and G.G.Yakobson, Izv.Akad.Nauk SSSR, Ser. Khim., 1981, 867.