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Organophosphorus Compounds in Reactions with Quinones

A.A.Kutyrev and V.V.Moskva

The results of studies on the chemical behaviour of organophosphorus compounds in reactions with quinones are surveyed. Attention is concentrated on discovering the trends and general characteristics of such processes.
The bibliography includes 134 references.

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I. INTRODUCTION

During the last quarter of a century, studies in the chemistry and technology of organophosphorus compounds have expanded greatly throughout the world, in many respects due to the growing needs for biologically active preparations, among which the aromatic esters of phosphorus acids play a leading role.

Until recently, there has been no reliable information about the reaction mechanisms and frequently also about the structure of the products of the interaction of organophosphorus compounds with quinones. Only the wide-scale application of modern physical research methods made it possible to solve some of these problems.[1-4] Nevertheless, a number of processes with participation of phosphorus(III) compounds do not fit within the framework of existing ideas[5] and the reactivities of compounds of pentacoordinate phosphorus in relation to quinones are not susceptible to prediction.

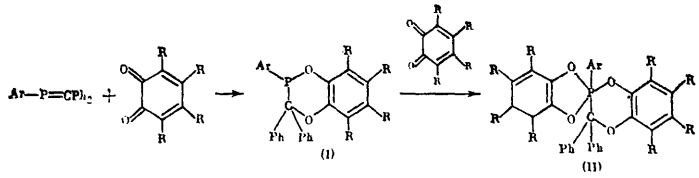
There are no publications in the literature of a review character on the interactions of phosphorus compounds with quinones. The monographs and reviews devoted to various aspects of the chemistry of organophosphorus compounds[6-10, 13,14] and quinonoid compounds[4,11,12] provide only disjointed descriptions of individual phosphorus-containing reagents in their reactions with certain quinones.

In the present review an attempt has been made to survey the experimental data on the synthesis, reactivities, and mechanisms of the reactions of organophosphorus compounds with quinones. The aim was not to discuss comprehensively all the reactions described in the literature but an attempt has been made to concentrate attention on the general characteristic features of these chemical reactions.

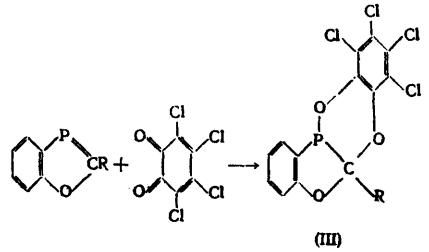
II. COMPOUNDS OF DICOORDINATE AND TRICOORDINATE PHOSPHORUS

1. Reactions of Phosphines and Related Compounds with Quinones

The study of the interaction of aryldiphenylmethylenephosphine with tetrachloro-1,2-benzoquinone, 3,5-di(t-butyl)-1,2-benzoquinone, and phenanthrenequinone showed that 1:1 cyclic [2+4] adducts (I) are formed in all cases. For a 1:2 ratio of phospha-alkenes and quinones, the main reaction products are phosphoranes (II):[15]



1,3-Benzoxaphosphole reacts with tetrachloro-1,2-benzoquinone to form the phosphinite (III):[16]



(III)

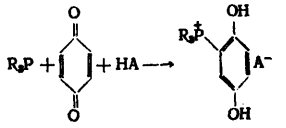
Tertiary phosphines readily react with quinones, forming products with P–O or P–C bonds,[17-20] whose structure is determined by the nature of the substituents in the quinone and the phosphine.

The addition of triphenylphosphine to *p*-benzoquinone leads to the phosphobetaine (IV):[4,17,18]

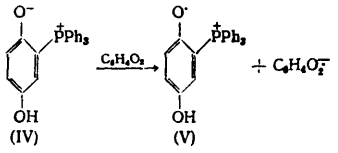


(IV)

This reaction has been used to obtain a whole series of quaternary phosphonium salts, which are used to promote the interaction of vicinal epoxides with phenols and carboxylic acids or their anhydrides in order to obtain polymer films:[19]

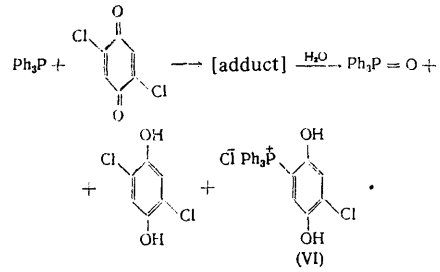


The oxidation of the phosphobetaine (IV) can afford the paramagnetic radical-cation (V):[10,18]



(IV) (V)

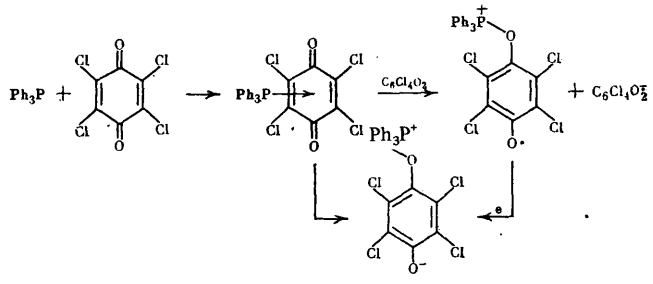
The interaction of triphenylphosphine with 2,5-dichloro-1,4-benzoquinone gives rise to an adduct, which is converted on treatment with water into diphenylphosphine oxide, 2,5-dichlorohydroquinone, and 2,5-dihydroxy-4-chlorophenyl(triphenyl)phosphonium chloride (VI):[20]



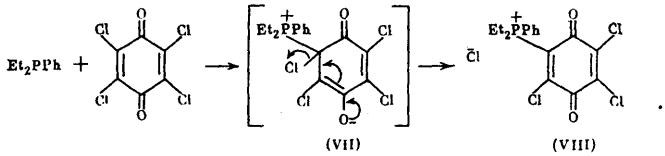
(VI)

The EPR spectrum of the 2,5-dichloro-1,4-benzoquinone–triarylphosphine system, with a complex hyperfine structure of the signals, indicates the formation of phosphorus-containing paramagnetic species.[35]

It has been demonstrated by UV and EPR spectroscopic methods that, in the reactions of triphenylphosphine with chloranil and also with bromoanil and iodanil, the paramagnetic products are formed mainly as a result of the oxidation by the quinone of phosphine–quinone charge-transfer complexes, but this is only one of the pathways leading to the final product:[17]

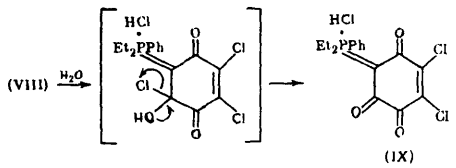


Diethylphenylphosphine reacts with chloranil to form the phosphorus-containing dipolar product (VIII), which is probably formed from the intermediate (VII):[21]



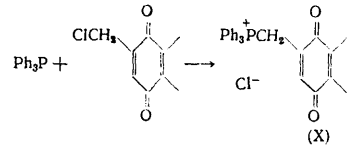
(VII) (VIII)

The chlorine atom in the *o*-position in the phosphabetaine (VIII) is readily substituted by a hydroxy-group from water, which leads to a new type of stable phosphorus ylides (IX):



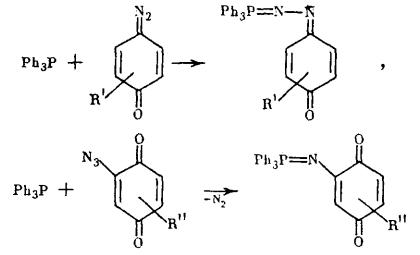
(IX)

The interaction of phosphines with quinones having a chloromethyl substituent has been described. The main product is the phosphonium salt (X):[22]

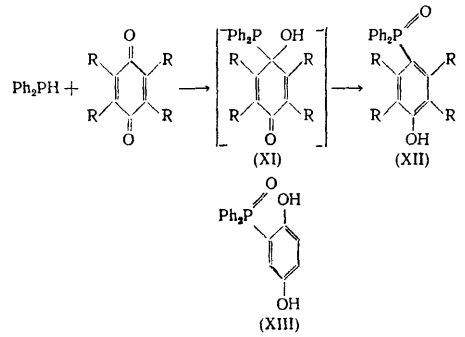


(X)

The adducts of phosphines with nitrogen-containing quinone derivatives also have a quinonoid structure:[4,23,24]

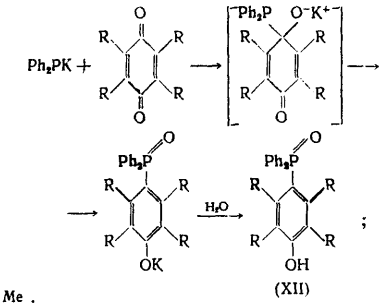


Secondary phosphines add to *p*-benzoquinones more vigorously than tertiary phosphines with formation of intermediates (XI) with a P–C bond, which are subsequently converted into the phosphine oxides (XII) [25] [however, according to other data,[26] the reaction product is compound (XIII)]:



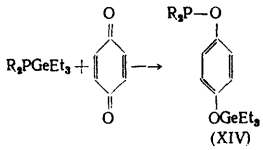
R = H, Cl .

The reaction apparently begins with nucleophilic attack by the phosphorus atom on the carbon of the carbonyl group.[25,27] It is accelerated with increase of the nucleophilicity of the phosphorus centre (for example, when hydrogen is replaced by an alkali metal[27]):



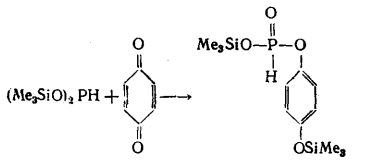
R = H, Me . (XII)

Dialkylgermylphosphine reacts with quinone via another mechanism. In this case the main product is *p*-triethylgermyloxyphenyl phosphinite (XIV)—a stable substance capable of being distilled, which was isolated from the reaction mixture in 50% yield:[28]

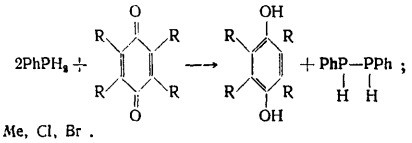


(XIV)

Silyl hypophosphites add to the 1,6-positions of *p*-benzoquinone without affecting the P–H bond:[29]

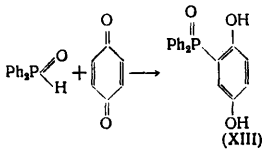


In contrast to secondary phosphines, primary phosphines do not add to quinones but reduce them to hydroquinones, being converted into diphosphines in this process:[30]



R = H, Me, Cl, Br.

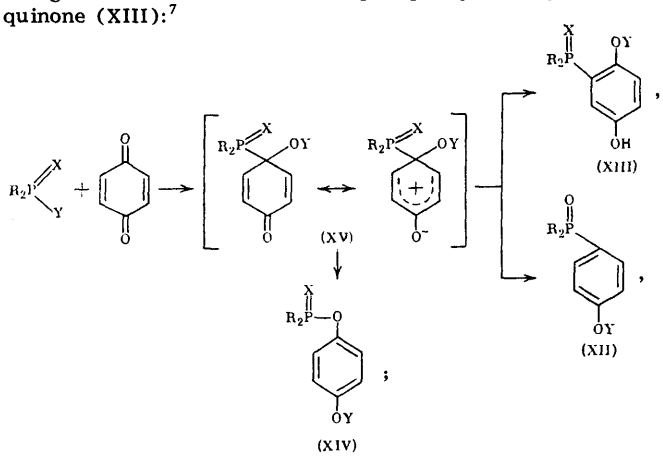
It is noteworthy that secondary phosphine oxides also react with quinones. The interaction of diphenylphosphinous acid with quinones leads to the *C*-phosphorylated adduct (XIII),[5,31] although, as will be shown below, almost all phosphorus-containing reagents having the general formula $R_2P(E)H$ (R = AlkO, ArO, or Alk_2N: E = O, NR′, or S) react with quinones to form *O*-phosphorylation products:



(XIII)

It is believed[5] that this anomaly is caused by the involvement in the reaction of the tautomeric form of diphenylphosphinous acid with tricoordinate phosphorus.

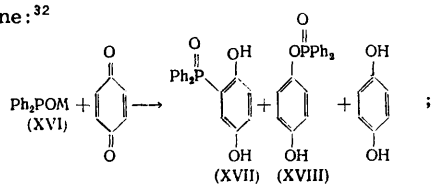
According to the views of other investigators, the intermediate (XV) is formed in this reaction and stabilised by being converted into the final *C*-phosphorylated hydroquinone (XIII):[7]



(XIII): R = Ar, X = O, Y = H; (XII): R = Ar, X = LEP (lone electron pair), Y = H, K; (XIV): R = Et, X = LEP, Y = GeR_3.

The characteristic features of the structure of the intermediate (XV) preclude the aromatisation process via the traditional deprotonation, since the ring carbon atom linked to the phosphorus group introduced contains no proton. Other pathways leading to the stabilisation of the cyclohexadienone, involving the migration of the phosphorus-containing group to the oxygen atom or a neighbouring carbon atom, are therefore followed.[7] Within the framework of the proposed scheme, one can also consider the mechanisms of the reactions of other organophosphorus compounds, namely diphenylphosphine, potassium diphenylphosphide,[25,27] and germylphosphine,[28] with *p*-quinones.

In contrast to diphenylphosphinous acid, its metal-substituted derivatives with *p*-benzoquinone to form both *C*- and *O*-phosphorylated products. For example, the phosphine oxide (XVII), the phosphinate (XVIII), and the hydroquinone in proportions of 1 : 1 : 1.5 and 1 : 0.5 : 1 have been isolated respectively in the reactions of lithium and magnesium salts of diphenylphosphinous acid (XVI) with *p*-benzoquinone:[32]



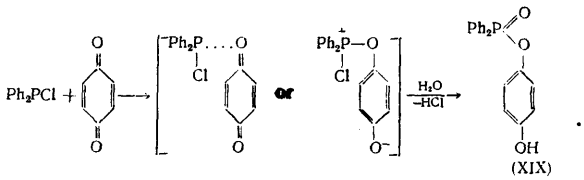
(XVII) (XVIII)

M = Li, MgCl.

The authors suggest that the phosphine oxide (XVII) is a result of the direct addition of the phosphinite (XVI) to a carbon atom of the quinonoid ring. The formation of two other products has been explained from the standpoint of the one-electron transfer mechanism.

In our view, the interaction can proceed via both the mechanism put forward by Koda et al.[32] and via the mechanism described above involving the initial addition of the phosphorus-containing reagent to a carbonyl group of the quinone and subsequent isomerisation of the intermediate (XV) to the *O*- and *C*-phosphorylation products.

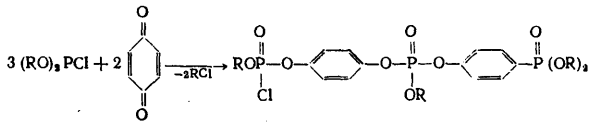
Chlorodiphenylphosphine reacts with quinone to form a 1 : 1 adduct to which the structure of a molecular or betaine-like complex has been attributed.[31] Treatment of the complex with water leads to the isolation of the *O*-phosphorylation product (XIX):



(XIX)

On the other hand, if the reaction is carried out in the presence of water, the *C*-phosphorylated hydroquinone (XIII) is formed. It is believed that chlorodiphenylphosphine hydrolyses to diphenylphosphinous acid, which is in fact the *C*-phosphorylating agent.[31]

Oligophosphates have been obtained in the reaction of dialkyl phosphorochloridites with 1,4-benzoquinone:[33]



Thus the interaction of phosphines with quinones involves the intermediate formation of charge-transfer complexes and the subsequent structural reorganisation leads to the final reaction products. The pathway resulting in stabilisation

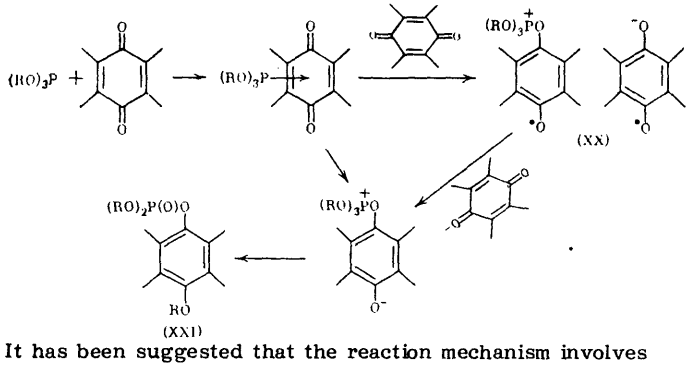
depends significantly on the nature of the substituents in the reactants and in many cases can be interpreted in terms of the theory of hard and soft acids and bases.[21,34]

The formation of tertiary phosphine oxides (XII) and (XIII) is characteristic of secondary phosphines and metal phosphides.

Primary phosphines do not add to p-quinones and an oxidation-reduction process takes place instead.

2. Reactions of Phosphites with *p*-Quinones

All phosphite esters interact with p-quinone via the 1,6-addition mechanism.[2,3,21,35] This pathway predominates among other possible reaction pathways, since it leads to stable aromatic phosphates (XXI):



It has been suggested that the reaction mechanism involves the formation of the radical-ion pair (XX), but other pathways leading to the final products are also possible.[10,17]

Trimethyl phosphite adds to monosubstituted *p*-benzoquinones, affording mainly the O-phosphorylated adducts (XXII) and (XXIII) and sometimes the phosphonates (XXIV) (Table 1):[2]

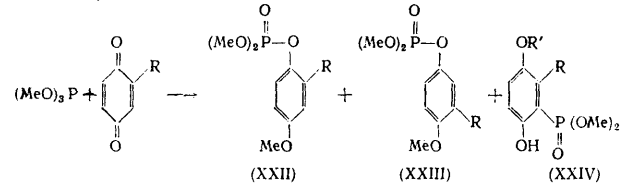
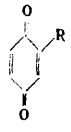


Table 1. The products of the reaction of trimethyl phosphite with *p*-benzoquinones.[2]

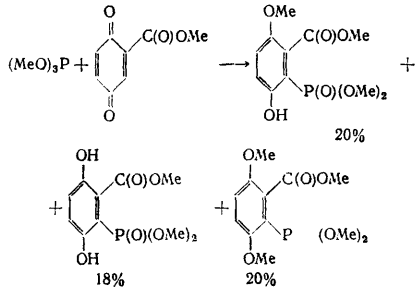


R	Yield of phosphate (XXII), %	Yield of phosphate (XXIII), %	Yield of phosphonate (XXIV), %*
OMe	79	2.5	—
Me	44	36	—
t-Bu	—	72	—
$SiMe_3$	—	67	—
CH_2OMe	17	50	—
Br	23	48	—
Cl	28	47	—
C(O)Ph	—	—	42
C(O)OMe	—	—	38

*The overall yield of the phosphonates (XXIV, R' = H and Me).

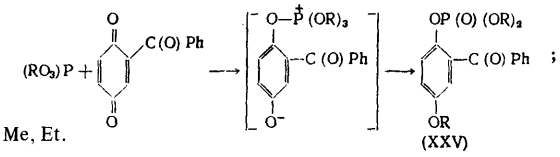
It has been established that the ratio of the phosphates (XXII) and (XXIII) is influenced by the nature of the substituent R. For example, the reaction with methoxy-*p*-benzoquinone produces mainly the 2-substituted aryl phosphate (XXII) and a small amount of the regioisomeric phosphate (XXIII). On passing to methyl-*p*-benzoquinone, the phosphorylation proceeds with a much lower degree of regioselectivity (Table 1). Nevertheless, t-butyl-*p*-benzoquinone and trimethylsilyl-*p*-benzoquinone react to form only the 3-substituted isomer (XXIII). Methoxymethyl-p-benzoquinone reacts with trimethyl phosphite to form the phosphates (XXII) and (XXIII) in proportions of 1 : 3, while in the reactions of bromo- and chloro-*p*-benzoquinones the products are in proportions of 1 : 2 (Table 1).

Only *C*-phosphorylated products have been detected in the reactions of trimethyl phosphite with quinones containing π-acceptor substituents. For example, phosphite reacts with methoxycarbonyl-*p*-benzoquinone to form phosphonates of type (XXIV):

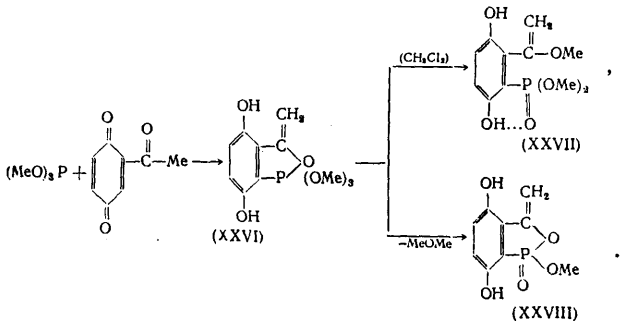


The interaction with benzoyl-*p*-benzoquinone proceeds analogously and results in the formation of products with the phosphonate structure.[2]

According to other data, the final product of the reactions of phosphites with benzoyl-*p*-benzoquinone is the aryl phosphate (XXV). It has been demonstrated by ^{31}P NMR that a dipolar intermediate arises in the initial stage of the reaction and that its stabilisation leads to the final phosphate (XXV):[36]



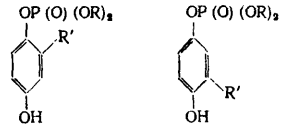
Acetylquinone reacts differently. It has been established that the phosphorane (XXVI) formed initially rearranges in CH_2Cl_2 to the methyl ester (XXVII). In other solvents, the phosphorane (XXVI) is converted into the cyclic phosphonate (XXVIII):[36]



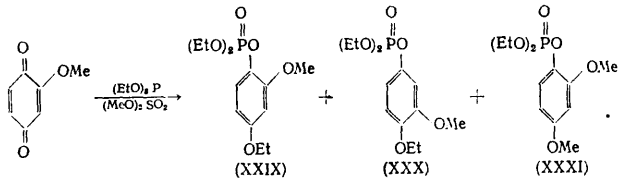
Since the product-determining stage of the reactions of phosphites with quinones is the intramolecular transfer of the alkyl substituent from the phosphorus atom to the oxygen

atom in the *p*-position in the betaine intermediate, the addition of electrophiles to the reaction mixture can lead to the synthesis of non-traditional final compounds.

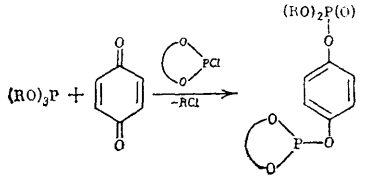
This type of result can be achieved when a source of protons is employed.[37] However, the method is not applicable to all quinones. Chlorotrimethylsilane is a more effective trapping agent. The reactions of quinones with the two-component phosphite/chlorotrimethylsilane system lead, after hydrolysis, to the formation of *p*-hydroxyaryl phosphates as the main product:[37]



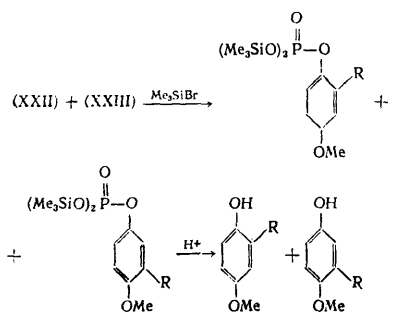
Dimethyl sulphate is yet another trapping agent. However, the reaction of triethyl phosphite with methoxy-*p*-benzoquinone in the presence of dimethyl sulphate affords the 4-ethoxyphosphates (XXIX) (49%) and (XXX) (12%). The yield of the expected 4-methoxyphosphate (XXXI) is only 5%:[37]



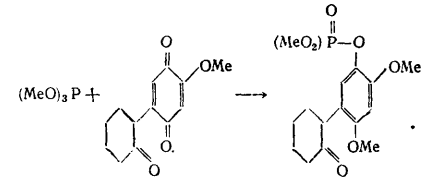
If cyclic phosphorochloridites are used as the trapping agents, then the products of the interaction of phosphites with *p*-benzoquinone are diphosphorylated hydroquinones. The compounds synthesised have many useful properties, in particular they impart fire resistance to materials:[38]



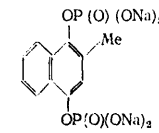
The hydrolysis of aryl dimethyl phosphates (XXII) and (XXIII) by refluxing in the $NaOH/H_2O/ROH$ mixture or water in the presence of catalysts comprising a caesium fluoride[39] and the potassium fluoride cyclohexyl-18-crown ether system[40] gives rise to poor results, which may be a consequence of the tendency of electron-saturated dialkylphosphorylphenols to be oxidised, especially in basic media. The hydrolysis is more successful if the phosphates are subjected to preliminary dealkylation with bromotrimethylsilane and are converted into the corresponding silyl phosphates:[40]



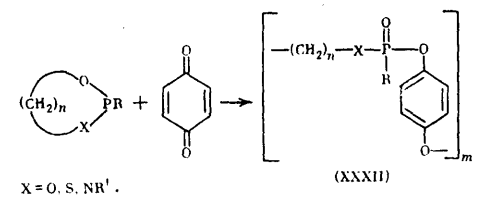
The interest in the reactions of phosphites with quinones has been aroused by the possibility of synthesising practically useful products, in particular biologically active preparations. The most convenient method of synthesis of 2-arylcyclohexanones, which are the basic compounds for the manufacture of the antibiotic "lysolipin I", is apparently based on this reaction:[2,41]



The tetrasodium salt of 2-methyl-1,4-naphthylene diphosphate, obtained from phosphite and 2-methyl-1,4-naphthoquinone, is one of the few radiosensitising agents for the radiotherapy of malignant tumours.[42] At a concentration of 4×10^{-6} M, this compound causes 50% suppression of mitosis in living tissues. It has been suggested that the action of this preparation consists in blocking the synthetic processes in cells associated with phosphorylation. It is noteworthy that the preparation itself has no therapeutic effect on malignant tumours.[42]

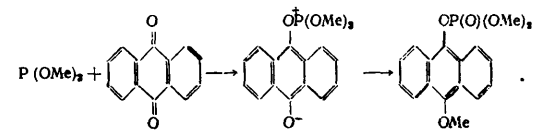


The synthesis of many industrial materials is based on the reactions of phosphites with quinones. For example, aromatic half-esters having the general formula $(OAr)_n$, used for the manufacture of moulded articles, adhesives, and fire extinguishing agents,[43] are formed by the reaction of substituted and unsubstituted quinones with compounds of tervalent phosphorus of the type $(RO)_2PR'$, while mixtures of cyclic phosphites and *p*-benzoquinone produce the polymers (XXXII), which have been used successfully as adhesives, plasticisers, and modifying agents reducing the combustibility of various chemical products:[44]

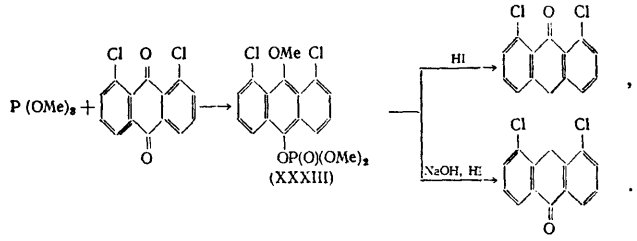


X = O, S, NR'.

Under severe conditions, trimethyl phosphite is capable of adding to anthraquinone. The reaction mechanism includes two stages: the appearance of a dipolar intermediate and its isomerisation to the final 10-methoxy-9-dimethylphosphorylanthracene:[45]

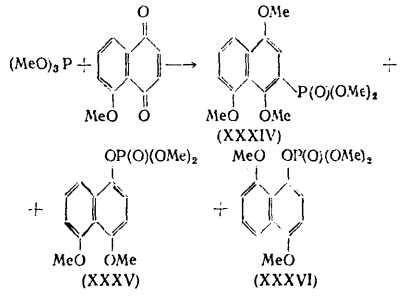


In the case of 1,8-dichloroanthraquinone, the relatively bulky phosphorus-containing residue enters the less hindered 10-position, while the methyl group enters the 9-position, forming the adduct (XXXIII):

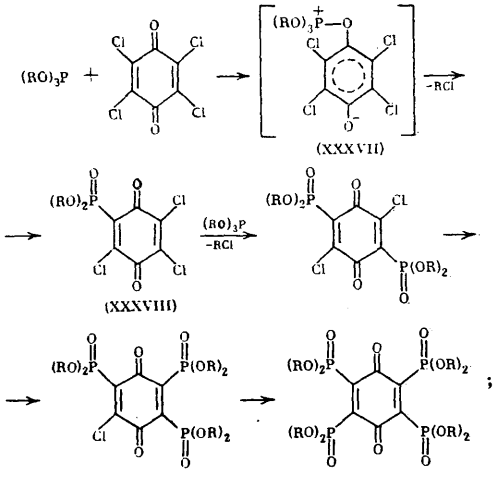


Selective hydrolysis of the methoxy- and phosphoryloxy-groups of the phosphate (XXXIII) and subsequent reduction of the hydrolysis products by hydriodic acid makes it possible to synthesise 1,8- and 4,5-dichloroanthrones which are otherwise difficult to obtain.[45]

The reactions of phosphites with naphthoquinones are less regioselective. Treatment of *O*-methyljuglone[5-methoxy-1,4-naphthoquinone] yielded all three possible isomeric products, the overall yield of the phosphates (XXXV) and (XXXVI) being lower than the yield of the phosphonate (XXXIV):[2]

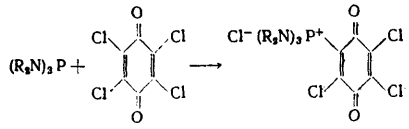


The reactions of phosphites having bulky alkyl substituents sometimes lead to unexpected results, in contrast to phosphites with unbranched substituents. Thus, instead of the usual addition to the quinone, the interactions of triisopropyl and triisobutyl phosphites with chloranil entail the substitution of the chlorine atoms in chloranil by phosphoryl groups. It has been suggested that the anomalous course of the reaction is caused by the steric hindrance of the dipolar intermediate (XXXVII), which is stabilised via the intramolecular Arbuzov reaction, affording the monophosphorylated quinone (XXXVIII). The latter reacts with the initial phosphite with successive substitution of the residual chlorine atoms in the quinone by phosphoryl groups:[46]

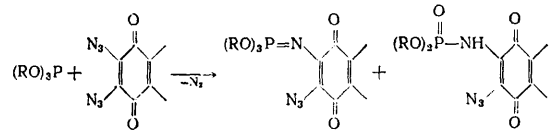


R = iso-Pr, iso-Bu.

Similar processes take place also in phosphorous triamides,[47] but in this system only one chlorine atom is substituted:

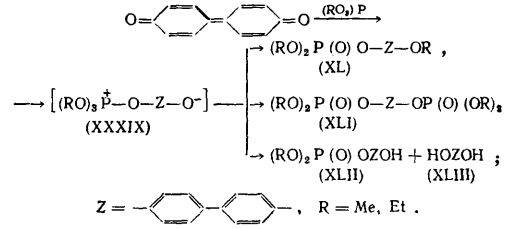


Trialkyl phosphites as well as phosphines react with azidoquinones. Although they are in the last place in the reactivity series of phosphoramidites (trialkylphosphines > triarylphosphines > trialkyl phosphites), nevertheless it is possible to isolate the products of their reactions with 2,3-diazidoquinone:[4,48]



Triaryl and trialkyl phosphorothioites do not react with azidoquinones.

The reactions of the full phosphite esters with diphenoquinone have been investigated in detail:[49]



4-Alkoxy-4′-biphenylyl dialkyl phosphate (XL), 4,4′-biphenylylene tetra-alkyl bisphosphate (XLI), dialkyl 4-hydroxy-4′-biphenylyl phosphate (XLII), 4,4′-dihydroxybiphenyl (XLIII), and the product of the self-polymerisation of diphenoquinone were isolated from the reaction mixture (Table 2).

Table 2. Yields of the products of the reaction of $(RO)_3P$ with diphenoquinone.[49]

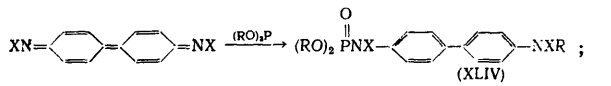
R	Yields of products, %				
	(XL)	(XLI)	(XLII)	(XLIII)	Diphenoquinone polymer
Me	15	15	7	15	35
Et	17	15	5	*	50

*The yield was not accurately established.

The author suggests the following reaction mechanism. Initially there is nucleophilic addition of the phosphite to diphenoquinone with formation of the intermediate dipolar adduct (XXXIX), which subsequently rearranges to the phosphate (XL). According to the authors, the rearrangement proceeds via an intermolecular mechanism: the phenoxide oxygen of one molecule attacks the alkyl residue of another. When the object of attack by the phenoxide oxygen is the phosphorus atom, the process then terminates with formation of the bisphosphate (XLI). Owing to the inevitable presence

of moisture, the adduct (XXXIX) hydrolyses and affords the phosphate (XLII) and dihydroxybiphenyl (XLIII). Together with the main reaction of the phosphite with diphenoquinone, another parallel reaction takes place—the polymerisation of diphenoquinone catalysed by the organophosphorus compound.

The products of the reactions of phosphites with diphenoquinoneimides are the phosphoramidates (XLIV), which have been isolated quantitatively:[49]

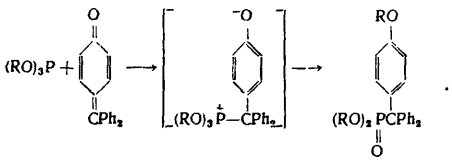


(XLIV)

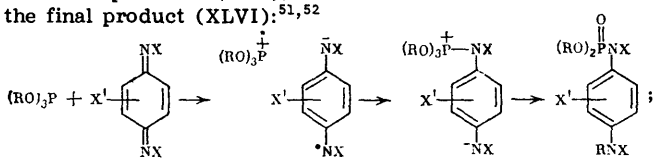
X = SO_2Me, SO_2Ph; R = Me, Et.

The reactivity of quinones in reactions with nucleophiles, including compounds of tricoordinate phosphorus, is determined both by the usual parameters (substituent, solvent, catalyst, etc.) and by specific parameters characteristic only of quinonoid systems. The latter include the oxidation-reduction properties of quinones. The redox potential of diphenoquinone (954 mV) is much higher than the potentials of "simple" quinones, for example chloranil (712 mV) or *p*-benzoquinone (696 mV).[4] This is in fact used to explain the significant differences between the reactions of phosphites with diphenoquinone.[49]

By virtue of the high electron-donating capacity of full phosphite esters, it is possible to achieve the reaction of quinonemethides with them. Fuchsone reacts with trialkyl phosphates on heating to form 1:1 adducts. As in most cases of the phosphorylation of *p*-quinones, in this instance the mechanism involves 1,6-addition to the conjugated bond system:[50]



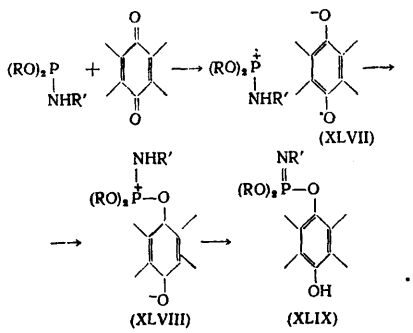
The reaction with 1,4-benzoquinonebis-sulphonylimine begins with a one-electron transfer stage involving the formation of the phospite radical-cation and the quinonediimine radical-anion, whose interaction leads to the intermediate dipolar ion (XLV), which is transformed further into the final product (XLVI):[51,52]



R = Alk, X = SO_2R', X' = H, Cl.

(XLV) (XLVI)

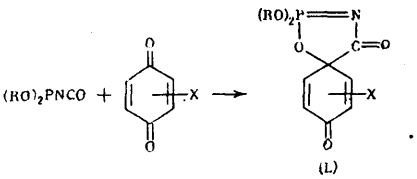
The amides of dialkylphosphorous acids readily interact with *p*-quinones, affording dialkyl *p*-hydroxyaryl *N*-organylphosphorimidates (XLIX):[53]



(XLVII) (XLVIII) (XLIX)

The signals of the chloroanil radical-anion and the phosphite radical-cation can be detected in the EPR spectra of the reaction mixture of *N*-acetylphosphoramidite and chloranil. A reaction mechanism has been proposed involving the initial formation of the radical-ion pair (XLVII), whose reaction via the stage involving the dipolar intermediate (XLVIII) leads to the final product (XLIX).[53]

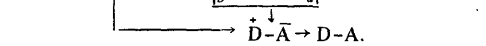
The interaction of *p*-benzoquinone with dialkyl phosphoroisocyanatidites is unusual: cycloaddition with participation of the carbonyl group in the quinone affords crystalline sparingly soluble oxazaphosphaspirocyclohexadienones (L):[54]



(L)

In the general case the interaction of compounds of tricoordinate phosphorus with *p*-quinones and their derivatives can be considered from the standpoint of one-electron transfer between the donor (D), i.e. the phosphorus(III) compound, and the acceptor (A), i.e. the *p*-quinone. This process is arbitrarily divided into three stages:[55] (1) the stage involving partial electron transfer (the formation of a charge-transfer complex); (2) the stage with total charge transfer (the formation of a radical pair in a solvent "cage"); (3) the stage involving the formation of fairly stable products (recombination or the emergence of the products from the "cage").

The following process mechanism can be put forward for the reactions of phosphorus(III) compounds with quinones:



Complexes [D → A] with partial electron transfer are formed initially and are followed by complexes [$D^{\ddagger}$ + $A^{\bar{}}$] with complete electron transfer. The radical-ion pair then emerges from the solvent "cage" and the free paramagnetic radical-ions $D^{\ddagger}$ and $A^{\bar{}}$ appear and in many cases can be detected by chemically induced dynamic nuclear polarisation (CIDNP) and electron paramagnetic resonance (EPR) methods. The recombination of the radical species via pathway *a* or *b* leads to the dipolar structures $\overset{+}{D}-\overset{-}{A}$, which in the case of phosphines are the final reaction products. The betaines $\overset{+}{D}-\overset{-}{A}$ can also be stabilised directly starting with the complex [D → A], by-passing the one-electron transfer stage.[10] The majority of the processes occurring in the phosphite (phosphine)—*p*-quinone system fit within the framework of the proposed mechanism.

3. The Reactions of Tricoordinate Phosphorus with *o*-Quinones

The polarographic method has been applied to the study of electron affinities of various quinones (Table 3).

When a number of *o*- and *p*-quinones were reduced, two one-electron reduction stages with fairly different half-wave potentials were observed.

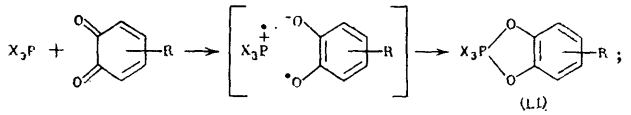
The data in Table 3 permit the following conclusions: firstly, *o*- and *p*-quinones have similar electron affinities and one-electron transfer with the intermediate formation of radical-ions is therefore also possible for the reactions of *o*-quinones; secondly, the smaller difference between the

first and second half-wave potentials ΔE for o-quinones compared with p-quinones shows that the transition from the one-electron mechanism to the two-electron mechanism is easier for o-quinones than for p-quinones.[56]

Table 3. Polarographic characteristics of the reduction of quinones.[56]

Quinone	$E'_{1/2}$, V	$E''_{1/2}$, V	$\Delta E = E''_{1/2} - E'_{1/2}$
Chloranil	−0.25	−1.17	−0.92
p-Benzoquinone	−0.56	−1.53	−0.97
Naphthoquinone	−0.81	−1.70	−0.89
Tetrabromo-o-benzoquinone	0.15	−0.57	−0.72
Tetrachloro-o-benzoquinone	−0.25	−0.61	−0.36
9,10-Phenanthrenequinone	−0.60	−1.23	−0.63
4,5-Dimethoxy-1,2-benzoquinone	−0.70	−1.20	−0.50

It has been established that both phosphines and phosphites react with o-quinones, affording adducts with the phosphorane structure (LI):[3,13,57]



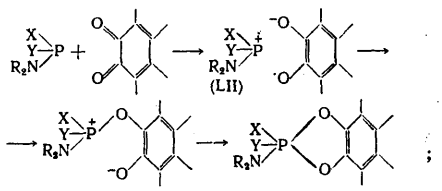
(LI)

X = Alk, Ar, AlkO, ArO, Cl.

A process mechanism incorporating a one-electron transfer stage, analogous to the mechanism of the reactions of phosphorus(III) compounds with p-quinones examined previously, has been proposed on the basis of kinetic and spectroscopic data.[58]

Phosphorus trichloride interacts with tetrachloro-o-benzoquinone, 9,10-phenanthrenequinone, 4,6-di(t-butyl)-1,2-benzoquinone, and 1,2-naphthoquinone, forming trichloro-1,2-phenylenephosphoranes (LI). A characteristic doublet signal, due to the interaction of the unpaired electron with the phosphorus nucleus, can be observed in the EPR spectra of the reaction mixtures, which indicates the possibility of the appearance of phosphorus-containing radical-ion species in the course of the reaction.[59]

EPR study of the interaction of phosphoramidites with tetrachloro-o-benzoquinone showed that the o-chloranil radical-anion and the phosphoramidite radical-cation (LII) exist for a time in the reaction mixture. The authors suggested that involvement of these species in the formation of the dipolar intermediate (LIII), which is converted into the final phosphorane (LIV):[56,57]

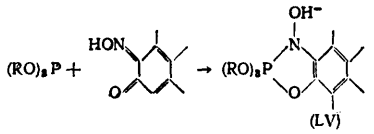


(LII) (LIII) (LIV)

X = OR', NR_2; Y = OR', NR_2, R = Alk.

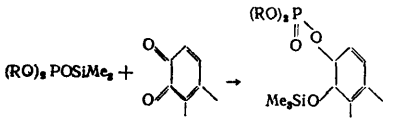
Phosphoramidites interact analogously with tetrabromo-o-benzoquinone. The one-electron transfer mechanism does not operate in all the reactions of 9,10-phenanthrenequinone, which has a smaller electron affinity (see Table 3), with phosphoramidites. On passing to 4,5-dimethoxy-1,2-benzoquinone, which is a still weaker acceptor, the formation of paramagnetic species is never detected. This confirms the conclusion that the replacement of the one-electron mechanism by the two-electron mechanism is more probable for o-quinones than for p-quinones.

The overall mode of reaction of phosphites with o-quinones, leading to the formation of phosphorane adducts, persists also for o-quinone monoximes. On reaction with phenanthrenequinone monoxime, trialkyl phosphites give rise to cyclic nitrogen-containing phosphoranes (LV), from which the initial quinone oxime can be regenerated:[60]



(LV)

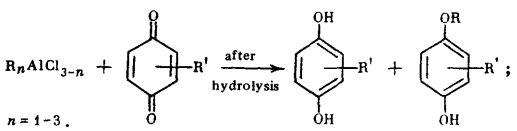
Silicon-containing phosphites react with o-quinones in the same way as with p-quinones, producing o-siloxyaryl phosphates:[61-63]



The absence from the given process of products with a pentacoordinate phosphorus atom is probably associated with their instability and ready isomerisation to aryl phosphates as a consequence of the high lability of the trimethylsilyl group.[14]

It is of interest to compare the reactivities of tricoordinate phosphorus compounds and other organoelemental nucleophiles in reactions with quinones. It has been established that the incompletely substituted alkyl(aryl)chloro(silanes) react on heating with p-benzoquinone in the presence of platinum catalysts, affording silyl ethers of hydroquinone.[64]

Hydroquinones and their monoalkyl ethers have been synthesised by the reaction of organoaluminium compounds with p-quinones and subsequent hydrolysis of the products:



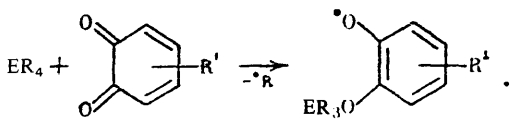
n = 1-3.

Paramagnetic intermediates—aluminium salts of semiquinone—were detected in the reaction of triethylaluminium and aluminium chloride with p-benzoquinone.[65]

2-Alkyl-3-chloro-1,4-naphthoquinones can be obtained from a mixture of trialkylaluminium with 2,3-dichloro-1,4-naphthoquinone. Similar naphthoquinones are formed in the reaction with participation of alkylzinc chlorides and tetra-alkylstannanes.[66] When gallium trichloride interacts with p-benzoquinone, 2:1 complexes are produced. The dipole moments for the formations of these compounds were determined by dielectric constant measurements.[67]

Thus organotin, organozinc, organoaluminium, and organosilicon, as well as organoantimony and organoarsenic compounds[68,69] do not add to p-quinones, in contrast to phosphorus(III) reagents, but convert them into alkylquinones, alkylhydroquinones, and hydroquinone ethers, the reactions requiring heating and the use of catalysts. However, despite the significant difference between the types of interaction of organophosphorus and other organoelemental compounds with p-quinones, the majority of the reactions proceed via a stage involving the formation of radical-ion species.[65,68,69]

The reactions of various metal halides with *o*-quinones have been studied in detail. The investigation of the EPR spectra of complexes of 1,2-naphthoquinone and 9,10-phenenthrenequinone with aluminium, gallium, and indium halides led to the conclusion that the compounds MX_3 exhibit electron-donating properties in relation to *o*-quinones. Electron transfer from the metal halides to the *o*-quinone molecule with formation of a paramagnetic chelate complex has been suggested.[70] Paramagnetic complexes were also obtained in reactions of *o*-quinones with organometallic compounds ER_4 (E = Sn, Si, or Ti; R = alkyl or halogen):

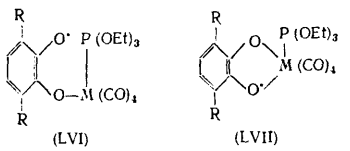


The reaction of tin tetrachloride with 3,6-di(t-butyl)-1,2-benzoquinone resulted in the formation of the *o*-benzosemiquinone complex, which a tetragonal pyramidal structure assigned on the basis of spectroscopic data.[71]

Evidently in their reactions with *o*-quinones organoelemental compounds having an unshared electron pair behave as electron-donating agents and, depending on the nature of the central atom and its environment, form cyclic or acyclic adducts.

In conclusion of this Section, devoted to a survey of studies on the reactions of phorphorus(III) compounds with quinones, the *o*-semiquinonoid complexes of metals with phosphite ligands must be considered.

The photolysis of metal decacarbonyls produces the radicals $M(CO)_5$ (M = Mn or Re),[72] whose interaction with *o*-quinones and triethyl phosphite leads to the appearance of the primary radical (LVI), which is converted further into the secondary radical (LVII):[73]



(LVI) (LVII)

M = Mn, Re; R = t-Bu.

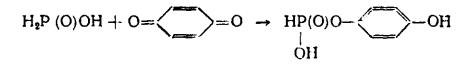
Kinetic measurements have shown that the rate of conversion ($k = 0.0013\ s^{-1}$) of the radical (LVI) into the radical (LVII) is appreciably lower than the rate of conversion ($k = 0.017\ s^{-1}$) of the analogous non-phosphorus radicals.[73] The large difference between the rate constants for the destruction of the primary radicals as a function of the presence of the phosphite ligand has been attributed to the influence of the electron-accepting properties of triethyl phosphite on the rate-limiting stage of the process.[74] It also follows from the EPR spectra that the substitution of a CO group by a triethyl phosphite molecule in the radical (LVI) and (LVII) shifts the electron density from the *o*-quinonoid ligand to the phosphorus atom.

A similar conclusion follows from the analysis of the electronic absorption spectra of complexes of types (LVI) and (LVII). It has been suggested that the shift of electron density as a result of exchange interactions between the phosphorus and oxygen atoms proceeds via the *d* orbitals of the metal atom by virtue of the coplanarity of these atoms.[73,75]

III. COMPOUNDS OF TETRACOORDINATE AND PENTACOORDINATE PHOSPHORUS

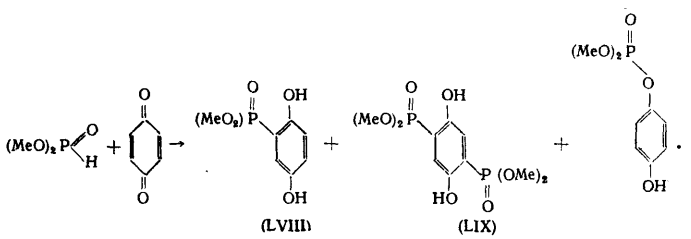
1. Reactions of Dialkyl Phosphites with Quinones

Almost all hydrophosphoryl compounds give rise to *O*-phosphorylation products in their reactions with quinones.[76-84,109] Hydrophosphites are no exception. The reaction of *p*-benzoquinone with 50% hypophosphorous acid results in the formation of reduction products—quinhydrone and hydroquinone, but, when this reaction is carried out in an anhydrous medium or in the presence of a small amount of water, an adduct, namely mono-*p*-hydroxylphenyl phosphite (yield up to 46%), is formed together with the benzoquinone reduction products:[76,77]



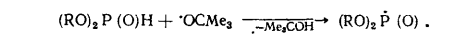
It has been established that dialkyl phosphites add to various *o*- and *p*-quinones, forming dialkyl hydroxyaryl phosphates.[78-84] The reaction is accelerated in the presence of bases, but can proceed also via a homolytic pathway.[7]

An exception to this general rule is the interaction of dimethyl phosphite with *p*-benzoquinone, which leads to the formation of the *C*-phosphorylated product (LVIII) and the *CC*-diphosphorylated product (LIX). An adduct having the phosphate structure has also been detected in the reaction mixture:[85]

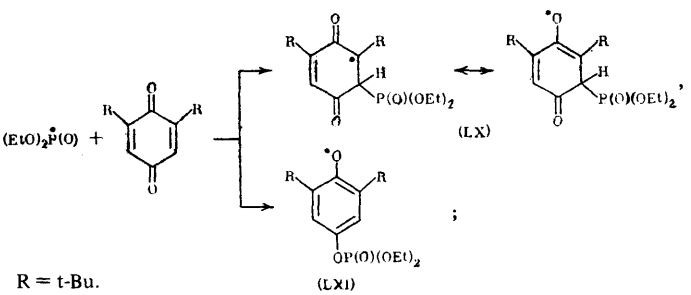


(LVIII) (LIX)

The photolysis of the corresponding hydrophosphoryl compounds in the presence of di(t-butyl) peroxide leads to the formation of phosphoryl radicals:[86]



These radicals add to 2,6-di(t-butyl)-1,4-benzoquinone, affording the phosphonate radical (LX) and the phosphate radical (LXI):[87]

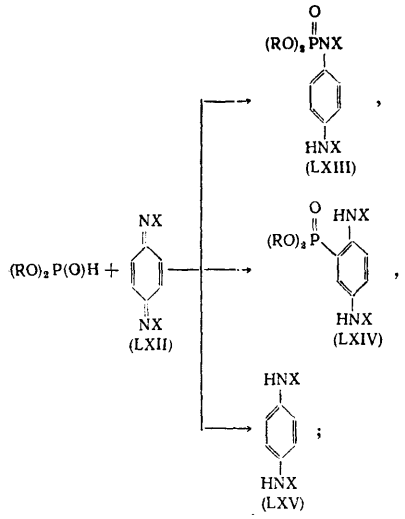


R = t-Bu. (LXI)

Species with an analogous structure are formed in the reactions of phosphonyl radicals with quinonemethides and 3,3,5,5-tetra(t-butyl)diphenoquinone.[87]

The synthesis of phenoxy-radicals of types (LX) and (LXI) by easy methods is a problem of current importance whose solution would lead to prospects for the synthesis of a wide variety of phosphorus-containing aromatic compounds.

Dialkyl phosphites react with *p*-benzoquinonebisbenzenesulphonylimine (LXII), forming a mixture consisting of the phosphoramidate (LXIII), the phosphonate (LXIV), and the bisamide (LXV):



R=Alk, X=SO_2Ph .

The yield of the compounds depends on the nature of the phosphite reagent, the molar ratio of the reactants, and the reaction conditions (Table 4).[88]

Table 4. The reaction of $(RO)_2P(O)H$* with *p*-benzoquinonebisbenzenesulphonylimine (LXII).[88]

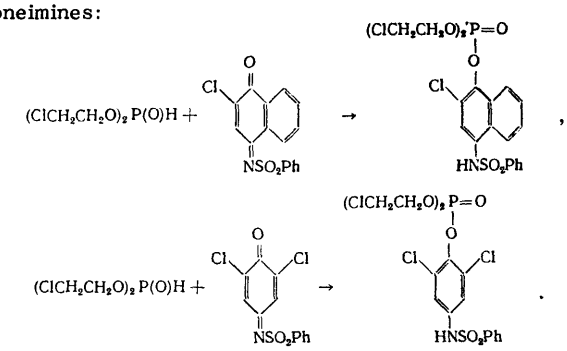
R	Solvent	*t*, °C	Duration, h	Yields of products, %		
				(LXIII)	(LXIV)	(LXV)
Me	—	25	48	25	40	30
Me	—	110	2	10	20	65
Me	—	140	2	10	15	70
Me**	—	100	3	—	—	>95
Me	benzene	25	72	20	45	30
Me	benzene	refluxing	10	20	30	45
Et	—	25	48	35	45	15
Et	—	110	2	20	25	50
Et	—	140	2	15	20	60
Et**	—	100	3	—	—	>95
Et**	benzene	refluxing	6	—	—	>95
изо-Pr	benzene	refluxing	4	—	>95	—

*The ratio $(RO)_2P(O)H$: (LXII) = 15 : 1.
**$(RO)_2P(O)H$ with a low purity.

All three products are obtained from dimethyl and diethyl phosphites, while diisopropyl phosphite gives rise to only the phosphonate (LXIV) (see Table 4). It has been noted that the quinoneimine (LXII) reacts with dialkyl phosphites only in the presence of a fifteenfold excess of the phosphite. If the amount of phosphite is less, then the reaction does not occur whatever the conditions. This is true only for freshly distilled dialkyl phosphites. When reagents with a low degree of purity are used, hydrolysis results in the formation of phosphorous acid, which has powerful reducing properties. Under these conditions, the main reaction product is the bisamide (LXV) (Table 4).

An increase of temperature and reaction time decreases the yields of the phosphorus compounds and increases the yield of the bisamide (LXV). The presence or absence of the solvent in the reaction mixture has almost no effect on the ratio of the reaction products.[88]

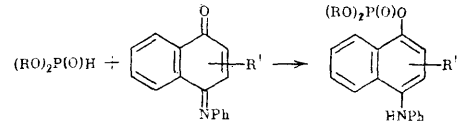
In order to obtain practically useful compounds, di(chloroalkyl) phosphites were introduced into the reaction with quinoneimines:



The resulting 2-chloro- or 2,6-dichloro-arene-4-sulphonamidoaryl di(chloroalkyl) phosphates have been recommended as additives to oils and fuels.

In contrast to the reactions of unsubstituted dialkyl phosphites, this process proceeds more vigorously, requiring a lower temperature to initiate the reaction.[89]

p-Quinone anils combine with dialkyl phosphites to form *O*-phosphorylated adducts:[84]

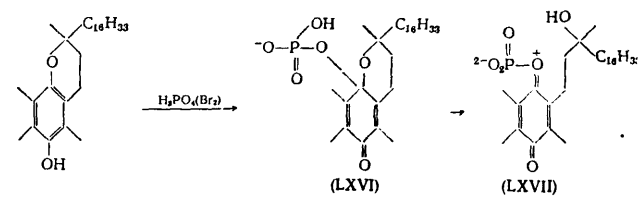


2. Reactions of Phosphates with Quinones

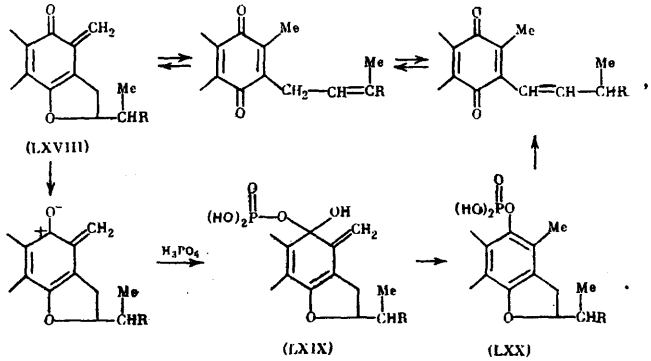
Many natural products, isolated from higher and lower plants and animals, belong to the class of quinones. They include dyes, growth regulators, antibiotics, and catalysts of respiratory processes. For example, juglone, detected in the roots and leaves of the walnut tree, exhibits a pronounced allelopathic activity, lawsone, the yellow pigment of henna leaves, is known as a fungicide, plumbagin, identified in the roots, stems, and leaves of certain tropical plants, is a mirobicide, and quinones of the vitamin K series, contained in micro-organisms and plants, are catalysts of the biosynthesis of certain proteins.[90]

The interest of chemists in the reactions of such natural products with various reagents, including organophosphorus reagents, is understandable, because such investigations are closely related to the synthesis of promising biologically active preparations.

It has been found that the product of the reaction of the natural terpene tocopherol with phosphoric acid tocopheroxide (LXVI), whose acetal phosphate group is capable of phosphorylating adenosine diphosphoric acid with formation of its triphosphoric acid analogue—the energy source in cell processes. The active principle is in this instance the quinonoid system (LXVII), which acts as a phosphorylating agent:[91]

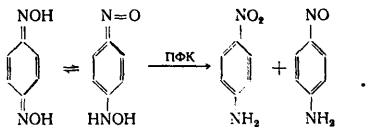


Phosphoric acid also adds to one of the active forms of vitamin K_1 (LXVIII) with formation of the phosphate (LXIX), which is subsequently reduced by flavin-nucleotide to the phosphate (LXX). On treatment with adenosine diphosphate and cytochrome, the latter gives rise to the initial quinone and adenosine triphosphoric acid:[92]

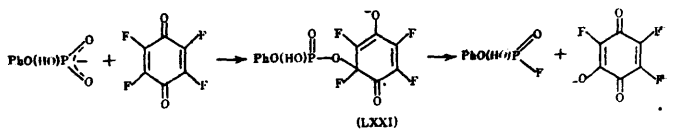


(LXVIII) (LXIX) (LXX)

It has been established that in the presence of an excess of polyphosphoric acid (PPA), quinone dioxime disproportionates with formation of *p*-nitroaniline and *p*-nitrosoaniline, which can be isolated respectively from diluted and neutralised solutions:[93]



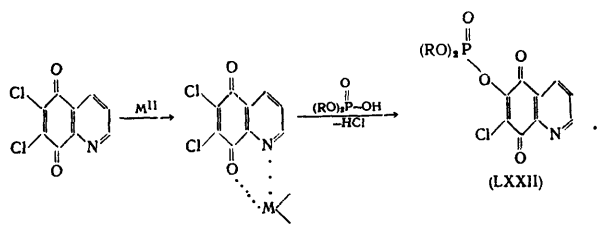
The anion of the phenyl ester of phosphoric acid, which is an active nucleophile, interacts with fluoranil. The fragmentation of the intermediate (LXXI) formed initially leads to the final reaction products:[94]



(LXXI)

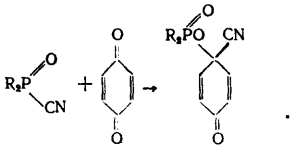
This reaction can be used as a method of synthesis of phosphorofluoridic acids.

Dialkylphosphoric acids do not interact with 6,7-dichloroquinoline-5,8-quinone, but in the presence of transition metal ions the reaction does occur. The products of the catalytic process are substituted quinolinequinones (LXXII). The activating effect of the metal ion has been explained by the increase of the deficiency of electron density at the C(6) atom, which promotes the substitution of the chloro-group in this position (as the chloride anion) by the phosphoryl group:[95]

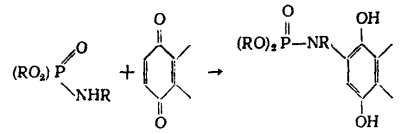


(LXXII)

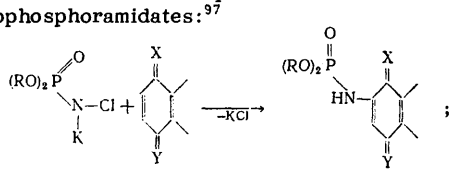
A rare variant of the nucleophilic addition to a C=O bond of the quinone occurs in the reactions of phosphinic acid cyanides with *p*-benzoquinone:[96]



Phosphoramidates having the N–H bond interact with quinones, forming phosphorylated 1,4-adducts:[47]



It has been established that quinoneimines can be aminated by *N*-chlorophosphoramidates:[97]

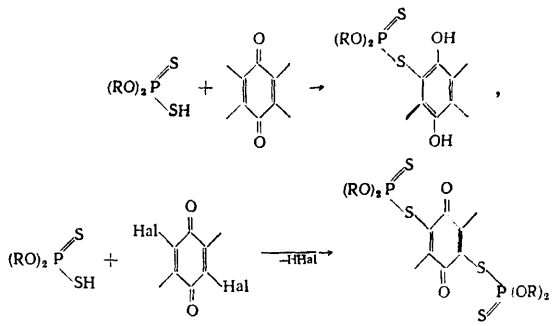


R=Ar, X=NSO_2Ar, Y=NSO_2Ar, O.

Among compounds of tetracoordinate phosphorus, sulphur-containing phosphates have been studied in greatest detail in their reactions with quinones because their preparative and kinetic investigation is easy.

The interaction of phosphorodithioates with quinones proceeds readily and fairly selectively in the absence of catalysts. The reaction products can be isolated from the reaction mixture quantitatively, do not require special purification, and their identification presents no difficulties. Phosphorodithioates and quinones are uncommonly suitable reactants for kinetic and spectroscopic studies. The advantages enumerated above as well as the ready availability and stability of the initial compounds have made the reactions of phosphorodithioic acids with quinones irreplaceable as objects of comprehensive and profound study.

Phosphorodithioic acids enter into addition[98] or substitution[99] reactions with quinones and their halogeno-derivatives:



The products have found applications in veterinary science and the pharmaceutical industry and are used as antioxidants and insecticides. As representatives of the class of phosphorodithioates, they are characterised by a broad spectrum of insectoacaricidal activity, rapidity of action, small consumption of the preparation per unit area treated, and the absence of toxic residues. They are most effective in the fight against insect species resistant to other organophosphorus insectoacaricides.[100]

It has been found that the silyl esters of phosphorodithioic acid are also capable of adding to *p*-quinones with formation of 1,4-addition products.[101]

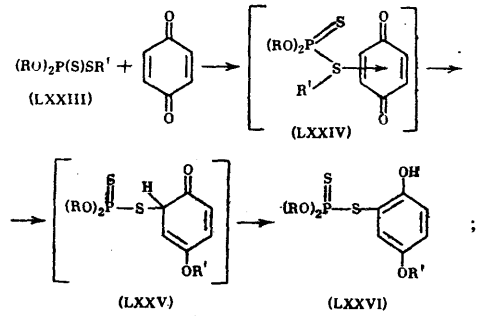
Spectrophotometric study of the reaction involving the addition of phosphorodithioic acids and silyl phosphorodithioates to *p*-benzoquinone showed that the rate of reaction is described by a second-order equation, of first order with respect to each reactant. Silyl phosphorodithioates are less reactive in heptane than the corresponding acids and the sensitivity of the reaction to the influence of substituents at the phosphorus atom is low. Whereas a tendency for the reaction to be accelerated with increase of the acidity of individual groups of dithio-derivatives of phosphorus (phosphates, phosphonates, and phosphinates) has been traced, overall there is no such trend. This may be a consequence of the important role of not only the acid but also the nucleophilic properties of phosphorodithioates in the addition reaction.[103]

An appreciable increase of the rate of reaction is observed in basic solvents. In the correlation equations taking into account the influence of the polarity, polarisability, and specific properties of the medium[102] on the rate of reaction of *OO*-diethylphosphorodithioic acid and its *S*-trimethylsilyl ester with *p*-benzoquinone, only the contribution of the nucleophilic solvation of the solvent is statistically significant.[103]

On passing to media with pronounced nucleophilic properties, the reactivity of silyl phosphorodithioates becomes comparable in terms of rate of reaction to that of phosphorodithioic acids.

In order to elucidate the cause of such relations, the deuterium kinetic isotope effects (KIE) have been investigated for phosphorodithioic acids and *p*-benzoquinone in various solvents. In all cases the "reverse" KIE is observed for the dithio-acids, which indicates an appreciable strengthening of the binding of the hydrogen atom in the transition state of the proton transfer stage from the phosphorus-containing reactant (LXXIIIa) to *p*-benzoquinone and may be a consequence of the fact that the activated complex has a structure resembling that of the intermediate (LXXV).[104]

When deuteriated *p*-benzoquinone was used, the KIE for the reaction with phosphorodithioates (LXXIIIa, b) in heptane and benzene proved to be unity, i.e. the migration of the ring proton takes place after the rate-limiting stage of the reaction. In basic media (dioxan, acetonitrile), where the KIE exceeds unity, the conversion of the intermediate (LXXV) into the product (LXXVI) becomes rate-determining. An analogous pattern of changes in the KIE for *p*-benzoquinone has been observed also in the reaction with *OO*-diethyl *S*-trimethylsilyl phosphorodithioate.

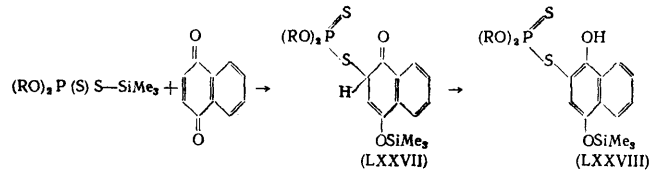


(a) R' = H (D); (b) R' = Si .

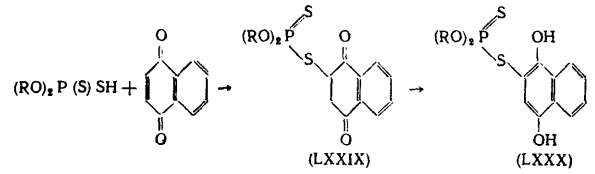
The set of data examined suggests that the addition of phosphorodithioates to *p*-benzoquinone proceeds in accordance with the scheme presented above. The fact that the same mechanism operates in the interaction of phosphorodithioic acids (LXXIIIa) and their *S*-trimethylsilyl esters (LXXIIIb) with quinone has been confirmed by the correlation between lg *k* for both processes in the media employed.[103]

In view of the high electron-accepting capacity of *p*-benzoquinone [105] and the appreciable nucleophilicity of the sulphur in phosphorodithioates,[106] the initial formation of a complex of the $n-\pi$ type (LXXIV) may be postulated. Its concentration and stability are evidently low, since it is not detected spectroscopically. This factor does not in its turn rule out the possibility of the reversal of the initial step of the interaction under certain experimental conditions. Next, the complex is converted endothermically into the intermediate (LXXV) and in weakly basic media this process is rate-determining, so the silyl phosphorodithioates are more reactive than phosphorus acids. The presence of the complex formation stage and the appearance of a late rate-limiting transition state explain the low sensitivity of the rate of reaction to the influence of substituents at the phosphorus atom and to the dielectric properties of the medium.[107] In markedly nucleophilic solvents, the transfer of the ring proton to the carbonyl group of the intermediate, (LXXV) → (LXXVI), becomes rate-determining and the reactivity of silyl phosphorodithioates is comparable, in terms of the rate of reaction, to that of phorphorus acids.

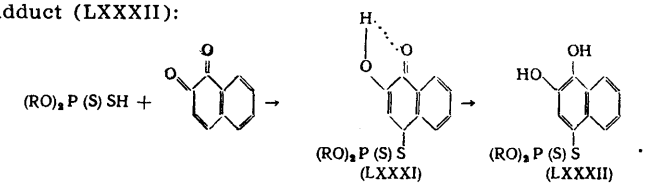
The interaction of phosphorodithioic acids and silyl phosphorodithioates with 1,4-naphthoquinone proceeds in accordance with a mechanism formally analogous to that in the reaction with *p*-benzoquinone. In the case of silyl phosphorodithioates, the 1,4-adduct (LXXVII) is formed as an intermediate, as in the reaction with *p*-benzoquinone:



However, it follows from the analysis of the time variation of the IR spectra of a mixture of solutions of 1,4-naphthoquinone and the dithio-acid that a product (LXXIX) of the addition to a C=C bond of the quinone is formed initially and is then gradually converted into dihydroxyphosphorothioylthionaphthalene (LXXX):[108]



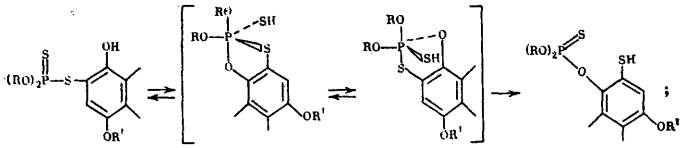
The reaction of phosphorodithioic acids with 1,2-naphthoquinone is unusual. The intermediate (LXXXI), detected by IR spectroscopy, isomerises over a period of time to the final adduct (LXXXII):



The stability of the enolic form of the intermediate (LXXXI) is apparently due to the energy gain by the system as a result of the formation of a stable intramolecular hydrogen-bonded complex.[108]

Thus the mechanism of the reactions of phosphorodithioic acids with quinones depends on the structure of the unsaturated reactant and involves the initial addition either to a C=C double bond or to the C=C – C=O conjugated system; silyl phosphorodithioates form initially 1,4-adducts in all cases.

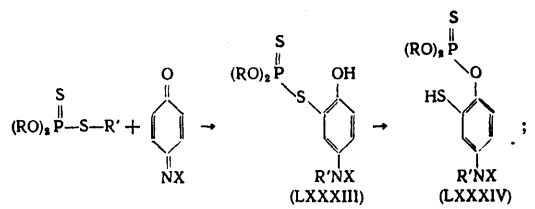
The final products of the reactions of phosphorodithioates with the *p*-quinones (LXXVI), (LXXVIII), and (LXXX) are capable of isomerising on heating to the corresponding phosphoromonothioates.[103,107] The mechanism of the rearrangement involves the intermediate formation of mercaptophosphoranes:



R'=H, $SiMe_3$.

Kinetic study of the isomerisation,[103,107] which takes place via a unimolecular mechanism, showed that the influence of the nature of the substituents at the phosphorus atom is determined by a set of electronic and steric factors and obeys the rules of the "hydroxyphosphorane concept".[110]

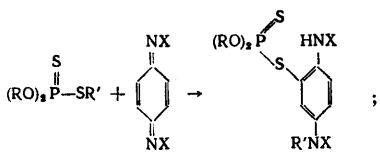
The interaction of phosphorodithioates with *N*-benzenesulphonyl-1,4-quinoneimine affords 5-(*N*-benzenesulphonamido)-2-hydroxyphenyl phosphorodithioates (LXXXIII), which isomerise to the corresponding phosphoromonothioates (LXXXIV):



(LXXXIII) (LXXXIV)

R'=H, $SiMe_3$; X=$SO_2C_6H_5$.

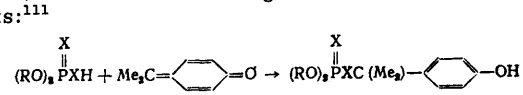
On passing to 1,4-quinonediimines, the reaction stops at the adduct (LXXXV) formation stage:[101]



(LXXXV)

R'=H, $SiMe_3$; X=SO_2Ph.

Phosphates and phosphorodithioates also add to quinonemethides, the reaction resulting in the formation of 1,6-adducts:[111]



X=O, S.

It is noteworthy that not only phosphorodithioic acids but also other organic compounds with a mobile hydrogen atom, for example, alcohols, amines,[4,12,112,113] mercaptans,[114,115] and carboxylic,[116] sulphinic, and sulphonic acids and their derivatives[117,118] react readily with quinones. The reductive aromatisation of the quinonoid systems is the driving force of these processes.

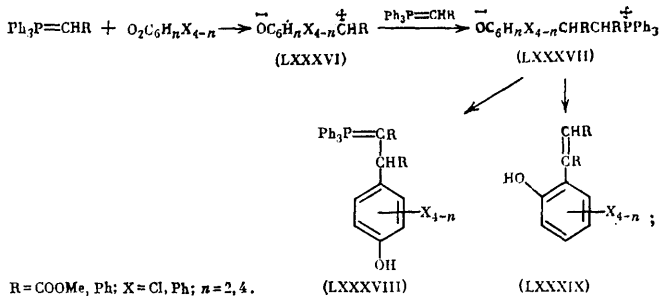
Comparison of the reactivities of phosphites and phosphates has shown that, apart from aromatisation, the formation of the extremely stable P=O bond promotes the reactions with quinones. This factor gives rise to process energetics such that in the case of phosphites addition in the 1,6-positions in the *p*-quinone takes place.

On the whole, *Ad* processes of this kind are encountered extremely rarely in the chemistry of *p*-quinones and occur only in certain cases.[78,119,120]

The structure of phosphates rules out the possibility of the formation of the phosphoryl group, so that the interaction with *p*-quinone follows the usual pathway and leads to the traditional 1,4-adducts, observed in the majority of reactions.

3. Reactions of Phosphoranes with Quinones

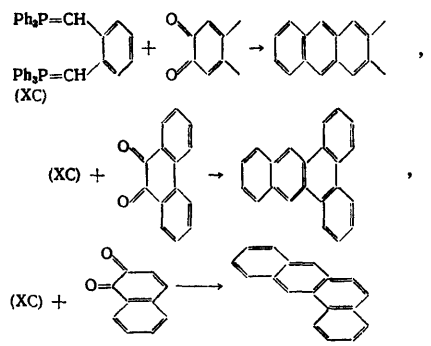
The quinonemethides (LXXXVI) are formed as intermediates in the reactions of alkylidenetriphenylphosphoranes with *o*- and *p*-quinones. They react with the initial phosphorane and give rise to the unstable betaines (LXXXVII). Depending on the substituents of the phosphorane component and in the ring, the betaines (LXXXVII) are either converted into the tautomer (LXXXVIII) or undergo the Hofmann degradation with formation of the olefin (LXXXIX):[121]



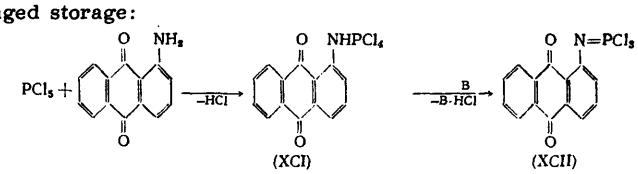
(LXXXVI) (LXXXVII) (LXXXVIII) (LXXXIX)

R=COOMe, Ph; X=Cl, Ph; *n*=2,4.

The reaction of *o*-phenylenebismethylenephosphorane (XC) with *o*-quinones can be used as a method of single-stage synthesis of complex carbocyclic aromatic compounds:[122]



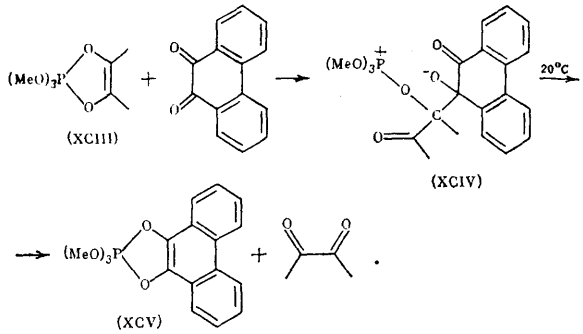
The interaction of phosphorus pentachloride with 1-aminoanthraquinone is of interest. It results in the formation of *N*-tetrachlorophosphoranyl-1-amino-anthraquinone (XCI)—a crystalline substance, which does not change after prolonged storage:



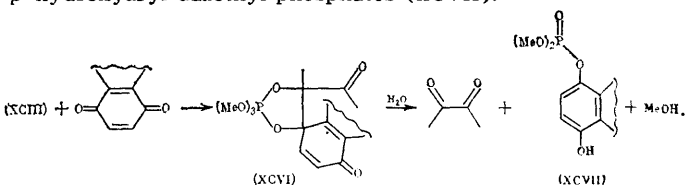
(XCI) (XCII)

Aminotetrachlorophosphoranes of the type $RNHPCl_4$ had been postulated earlier as intermediates in the reactions involving the phosphorylation of a wide variety of amines by phosphorus pentachloride. However, they were not isolated in a pure state. *N*-Tetrachlorophosphoranyl-1-aminoanthraquinone is the first representative of such compounds. Its stability may be associated with stabilisation by an intramolecular hydrogen bond. On treatment with tertiary bases, the phosphorane (XCI) is converted into trichlorophosphazoanthraquinone (XCII).[123]

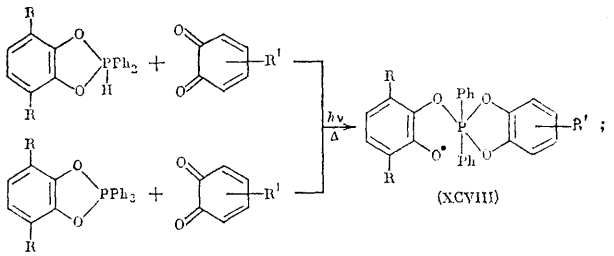
The dioxaphospholen (XCIII), obtained by the reaction of trimethyl phosphite with diacetyl, is capable of reacting with phenanthrenequinone. It has been suggested that the phospholen (XCIII), which exhibits a high phosphorylating activity, attacks the carbonyl group of phenanthrenequinone, which results in the formation of the dipolar adduct (XCIV).[124] At 20 °C, the adduct (XCIV) decomposes and the final products of reaction are diacetyl and the phosphorane (XCV):



The reaction of the phospholen (XCIII) with *p*-quinone leads to the formation of the phosphorane adducts (XCVI), which are unstable above 20 °C and whose hydrolysis affords *p*-hydroxyaryl dimethyl phosphates (XCVII):[124,125]



The interaction of [3,6-di(t-butyl)-1,2-phenylenedioxy]-diphenylphosphorane with *o*-quinones on exposure to UV radiation, gives rise to the radical species (XCVIII), which has also been obtained in reactions with participation of [3,6-di(t-butyl)-1,2-phenylenedioxy]triphenylphosphorane:[126]

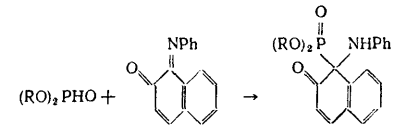


R = t-Bu.

It follows from the data examined that the reactions of phosphorus-containing reagents with quinones and quinonoid systems frequently lead to non-trivial and sometimes unexpected results. The knowledge of such reactions undoubtedly enriches theoretical organic chemistry, opens up new ways to the synthesis of compounds with unique structures which had been hitherto inaccessible, and also provides unlimited possibilities for obtaining a wide variety of substances with properties of practical value: polymeric materials, biologically active compounds, and medicinal preparations.

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During the preparation of the manuscript for printing, several interesting publications devoted to the interactions of organophosphorus compounds with quinones appeared in the literature. The results of a study of the reactions of dialkyl phosphites with sterically hindered *p*-quinones have been described.[127,128] The interaction takes place with the addition, usual in such cases, in the 1,6-positions of *p*-quinone with formation of adducts having the phosphate structure. An unusual reaction of dialkyl phosphites with the monoanil of *o*-naphthoquinone has been discovered.[129] Instead of the expected addition via the system of conjugated bonds of the anil X= C–C =Y, where X = C, O, or N and Y = O or N, with formation of phosphates, the reaction involving the rupture of the C=N bond and leading to the formation of adducts with the phosphonate structure takes place:



An analogous C=N bond rupture with retention of the remainder of the molecule has been found in the interaction of dialkyl phosphites with the anil of a sterically hindered quinone.[128] Radical processes with participation of quinonoid and phosphorus-containing reagents have been investigated in two studies.[130,131] Lawesson reported a new reaction of the "Lawesson reagent", which is popular in the chemistry of organophosphorus compounds at the present time. On reaction with substituted and unsubstituted *p*-quinones of the benzene, naphthalene, and anthracene series, it forms in certain cases phosphorus- and sulphur-containing cyclic products of a new type.[132] It has been shown[133] that the hydrazides of phosphoric acids react with *p*-benzoquinone in two ways: with formation of oxidation-reduction and condensation products. The operation of a particular reaction pathway depends on the expermental conditions.[133] The products of the interaction of phosphorus pentachloride with *p*-benzoquinone have been described.[134]

REFERENCES

1. M.A.A.Beg and M.S.Siddiqui, Pakistan J.Sci.and Ind.Res., 1970, 12, 334.
2. R.O.Duthaler, P.A.Lyle, and C.Heuberger, Helv. Chim.Acta, 1984, **67**, 1406.
3. F.Ramirez, Pure Appl.Chem., 1964, 9, 337.
4. C.Grudmann, in "Methoden der organischen Chemie (Houben–Weyl)", Georg Thieme, Stuttgart, 1977, Vol.VII/3a, pp.496, 643.
5. I.G.M.Campbell and I.D.R.Stevens, Chem.Comm., 1966, 505.
6. E.E.Nifant'ev, "Khimiya Fosfororganicheskikh Soedinenii" (The Chemistry of Organophosphorus Compounds), Izd.Moskov.Gos.Univ., Moscow, 1971.
7. E.E.Nifant'ev, "Khimiya Gidrofosforil'nykh Soedinenii" (The Chemistry of Hydrophosphoryl Compounds), Izd.Nauka, Moscow, 1983, p.104.
8. D.Purdela and R.Vilceanu, "Chemistry of Organophosphorus Compounds and Their Acid Derivatives" (Translated into Russian), Izd.Khimiya, Moscow, 1972, p.140.
9. A.J.Kirby and S.G.Warren, "The Organic Chemistry of Phosphorus" (Translated into Russian), Izd.Mir, Moscow, 1971.

10. Ya.A.Levin and E.I.Vorkunova, "Gomoliticheskaya Khimiya Fosfora" (The Homolytic Chemistry of Phosphorus), Izd.Nauka, Moscow, 1978, p.191.
11. C.Grudmann, "Methoden des organischen Chemie (Houben–Weyl)", Georg Thieme, Stuttgart, 1979, Vol.VII/3b, p.170.
12. S.Patai, "The Chemistry of Quinoid Compounds", John Wiley, London, 1974, Part 1, p.413.
13. R.F.Hudson, "The Structure and Mechanism in Organophosphorus Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1967, p.222.
14. G.A.Kutyrev and R.A.Cherkasov, Uspekhi Khim., 1984, **53**, 1675 [Russ.Chem.Rev., 1984(10)].
15. T.A.Kneap and F.Bichelhaupt, Tetrahedron, 1983, **39**, 3189.
16. J.Hoinicke and A.Tzschach, Tetrahedron Letters, 1983, **24**, 5481.
17. E.A.C.Lucken, F.Ramirez, V.P.Catto, D.Ruhm, and S.Derschowitz, Tetrahedron, 1966, **22**, 637.
18. E.A.C.Lucken, J.Chem.Soc., 1963, 5123.
19. US P.4093650 (1976).
20. F.Ramirez and S.Derschowitz, J.Amer.Chem.Soc., 1956, **78**, 5614.
21. F.Ramirez, D.Ruhm, and C.P.Smith, Tetrahedron, 1965, **21**, 1941.
22. V.N.Listvan, Zhur.Obshch.Khim., 1983, **53**, 1925.
23. L.Horner and H-G.Schmelzer, Chem.Ber., 1961, **94**, 1326.
24. US P.3387004 (1968); Chem.Abs., 1968, **69**, 77481.
25. A.N.Pudovik, G.V.Romanov, and V.M.Pozhidaev, Zhur.Obshch.Khim., 1977, **47**, 1910.
26. US P.3644530 (1968).
27. A.N.Pudovik, G.V.Romanov, and V.M.Poshidaev, Zhur.Obshch.Khim., 1978, **48**, 696.
28. J.Satge, C.Couret, and J.Escudie, Compt.rend.C, 1970, **270**, 351.
29. A.N.Pudovik, G.V.Romanov, and R.Ya.Nazmutdinov, Zhur.Obshch.Khim., 1979, **49**, 1942.
30. A.N.Pudovik, G.V.Romanov, and V.M.Pozhidaev, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1660.
31. I.M.Magdeev, Ya.A.Levin, and B.E.Ivanov, Zhur. Obshch.Khim., 1972, **42**, 2415.
32. K.Koda, H.Gomi, M.Ioschifuji, and N.Inamoto, Bull. Chem.Soc.Japan, 1974, **47**, 2453.
33. T.Kh.Gazizov, A.M.Kibardin, I.V.Gorokhovskaya, and A.N.Pudovik, Zhur.Obshch.Khim., 1978, **48**, 2374.
34. F.Basolo and R.G.Pearson, "Mechanisms of Inorganic Reactions" (Translated into Russian), Izd.Mir, Moscow, 1971, p.27.
35. E.Muller, H.Eggenspreger, B.Teissier, and K.Scheffler, Z.Naturforsch., 1963, **18b**, 984.
36. B.A.Arbuzov, N.A.Polezhaeva, and V.S.Vinogradova, Dokl.Akad.Nauk SSSR, 1971, **201**, 91.
37. J.S.Meek and L.Koh, J.Org.Chem., 1970, **35**, 153.
38. US P.3725510 (1973).
39. K.K.Ogilvie, S.L.Beaucade, N.Theriault, and D.W.Entwistle, J.Amer.Chem.Soc., 1977, **99**, 1277.
40. J.Szewczyk, B.Lejczac, and P.Kafarski, Synthesis, 1982, 409.
41. M.Dobler and W.Keller-Schierlein, Helv.Chim.Acta, 1977, **60**, 178.
42. B.C.Saunders, "The Chemistry and Technology of Organic Compounds of Phosphorus and Fluorine" (Translated into Russian), Inostr.Lit., Moscow, 1961, p.259.
43. Japanese P.5649332 (1981); Ref.Zhur.Khim., 1982, **9S446**.
44. Japanese P.2352 (1971); Ref.Zhur.Khim., 1971, **22S338**.
45. M.V.Gorelik, "Khimiya Antrakhinonov i Ikh Proizvodnykh" (The Chemistry of Anthraquinones and Their Derivatives), Izd.Khimiya, Moscow, 1983, p.124.
46. F.T.Reetz, US P.2935518 (1960); Chem.Abs., 1960, **54**, 19598.
47. D.B.Denhey and A.D.Pendse, Phosphorus and Sulfur, 1978, **5**, 249.
48. W.L.Mosby and M.L.Silva, J.Chem.Soc., 1965, 2727.
49. M.M.Sidky, M.R.Mahran, and Y.O.El-Khoshmieh, Tetrahedron, 1974, **30**, 47.
50. Yu.G.Shermolovich, L.N.Mirkovskii, Yu.A.Kopel'tsiv, and V.T.Kolesnikov, Zhur.Obshch.Khim., 1980, **50**, 811.
51. M.M.Sidky and M.F.Zayed, Tetrahedron, 1972, **28**, 5157.
52. A.P.Avdeenko and V.G.Koshechko, Zhur.Obshch. Khim., 1974, **44**, 1459.
53. A.N.Pudovik, E.S.Batyeva, A.V.Il'yasov, V.D.Nesterenko, A.Sh.Mukhtarov, and N.P.Anoshina, Zhur. Obshch.Khim., 1973, **43**, 1451.
54. I.V.Konovalova, L.A.Burnaeva, N.M.Kashtanova, and A.N.Pudovik, Zhur.Obshch.Khim., 1982, **52**, 1965.
55. I.M.Sosonkin, Symposium, "Mekhanizmy Geteroliticheskikh Reaktsii" (The Mechanisms of Heterolytic Reactions), Izd.Nauka, Moscow, 1976, p.106.
56. A.N.Pudovik, E.S.Batyeva, V.D.Nesterenko, A.V.Il'yasov, V.Z.Kondrashina, and V.I.Morozov, Zhur.Obshch.Khim., 1976, **46**, 1964.
57. A.N.Pudovik, E.S.Batyeva, V.D.Nesterenko, and E.I.Gol'dfarb, Zhur.Obshch.Khim., 1974, **44**, 1014.
58. J.Ogata and M.Jamashita, J.Org.Chem., 1973, **38**, 3423.
59. E.S.Klimov, A.A.Bumber, and O.Yu.Okhlobystin, Zhur.Obshch.Khim., 1983, **53**, 1739.
60. M.M.Sidky, M.F.Zayed, A.A.El-Kateb, and I.T.Hennawy, Phosphorus and Sulfur, 1981, **9**, 343.
61. A.N.Pudovik, E.S.Batyeva, and G.I.Zamaletdinova, Zhur.Obshch.Khim., 1972, **42**, 2577.
62. A.N.Pudovik, A.M.Kibardin, A.P.Pashinkin, Yu.I.Sudarev, and T.Kh.Gazizov, Zhur.Obshch. Khim., 1974, **44**, 522.
63. A.A.Kutyrev and V.V.Moskva, Zhur.Obshch.Khim., 1983, **53**, 2398.
64. I.I.Lapkin, D.N.Povarnitsina, V.V.Dvinskikh, and E.N.Rogozina, Zhur.Obshch.Khim., 1984, **54**, 1114.
65. Z.Florjanczyh and E.Szymanska-Zachara, J.Organomet.Chem., 1983, **259**, 127.
66. W.G.Peet and W.Tam, Chem.Comm., 1983, 853.
67. E.N.Gur'yanova, V.V.Muravlyanskii, I.P.Romm, V.D.Sviridov, and R.R.Shifrina, Zhur.Obshch. Khim., 1984, **54**, 817.
68. G.Retting and H.P.Latscha, Z.Naturforsch., 1983, **35b**, 399.
69. M.M.Sidky, M.R.Mahran, and W.M.Abdon, Phosphorus and Sulfur, 1983, **15**, 129.
70. E.S.Klimov, A.V.Lobanov, and D.A.Abakumov, Izv. Akad.Nauk SSSR, Ser.Khim., 1982, 2028.
71. A.I.Prokof'ev, Z.K.Kasymbekova, N.N.Bubnov, S.P.Solodovnikov, and M.I.Kabachnik, Izv.Akad. Nauk SSSR, Ser.Khim., 1982, 1275.
72. M.S.Wrighton and D.S.Ginley, J.Amer.Chem.Soc., 1975, **97**, 2065.
73. K.Sarbasov, B.L.Tumanskii, S.P.Solodovnikov, N.N.Bubnov, A.I.Prokof'ev, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 550.

74. M.I.Kabachnik, N.N.Bubnov, S.P.Solodovnikov, and A.I.Prokof'ev, Uspekhi Khim., 1984, **53**, 487 [Russ.Chem.Rev., 1984(3)].
75. S.P.Solodovnikov, K.Sarbasov, B.L.Tumanskii, N.N.Bubnov, A.I.Prokof'ev, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, 1982, **265**, 893.
76. V.I.Yudelevich, L.B.Sokolov, and B.I.Ionin, Zhur. Obshch.Khim., 1976, **46**, 2394.
77. V.I.Yudelevich, L.B.Sokolov, and B.I.Ionin, Uspekhi Khim., 1980, **49**, 92 [Russ.Chem.Rev., 1980(1)].
78. 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 the IInd Conference), Izd.Akad.Nauk SSSR, Moscow, 1962, p.203.
79. 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 the IInd Conference), Izd.Akad.Nauk SSSR, Moscow, 1962, p.207.
80. B.A.Arbuzov, N.A.Polezhaeva, and V.S.Vinogradova, Izv.Akad.Nauk SSSR, Otd.Khim., Nauk, 1960, 1218.
81. S.V.Bogdanov and S.V.Marochko, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 1960, **5**, 713.
82. V.A.Batyug, G.B.Sergeev, T.N.Saprykina, and B.M.Sergeev, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No.213-78, Moscow, 1979; Ref.Zhur. Khim., 1978, 9Zh316.
83. M.R.Mahran, W.M.Abdon, and T.S.Hafez, Egypt. J.Chem., 1981 (1982), **24**(4–6), 337.
84. M.M.Sidky and W.M.Abdon, Egypt.J.Chem., 1982 (1983), 25(4), 397.
85. E.K.Trutneva and Ya.A.Levin, Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 1684.
86. B.F.Roberts and K.U.Ingold, J.Amer.Chem.Soc., 1973, **95**, 3228.
87. R.N.Nasirov, B.L.Tumanskii, N.A.Malysheva, N.A.Kardanov, N.A.Godovikov, N.N.Bubnov, A.I.Prokof'ev, S.P.Solodovnikov, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 420.
88. M.M.Sidky, M.R.Mahran, and M.F.Zayed, Phosphorus and Sulfur, 1981, **9**, 337.
89. E.A.Titov, A.P.Avdeenko, and A.Ya.Mekh, Zhur. Obshch.Khim., 1972, **42**, 2577.
90. G.I.Zhungietu and L.A.Vlad, "Yuglon i Rodstvennye 1,4-Naftokhinony" (Juglone and Related 1,4-Naphthoquinones), Izd.Shtiintsa, Kishinev, 1978, p.6.
91. E.Bäuerlein and T.Wieland, Chem.Ber., 1969, **102**, 1299.
92. I.Chmelewska, Biochim.Biophys.Acta, 1960, **39**, 170.
93. E.Yu.Belyaev, E.I.Zagorodskii, and G.A.Suboch, Zhur.Org.Khim., 1984, **20**, 1116.
94. G.M.Kosolapoff and L.Maier, "Organic Phosphorus Compounds", Wiley Interscience, New York–London–Sydney–Toronto, 1973, Vol.6, Ch.19, p.321.
95. V.M.Clark, D.W.Huntchinson, A.R.Lyons, and R.K.Roschnik, J.Chem.Soc.C, 1969, 233.
96. L.Horner and R.Gehring, Phosphorus and Sulfur, 1981, **12**, 75.
97. M.M.Kremlev, N.P.Bezverkhii, A.V.Kharchenko, S.I.Shaposhnikov, and S.A.Ivonin, Article Deposited at UkrNIINTI, No.961-84, Dnepropetrovsk, 1984; Ref.Zhur.Khim., 1984, 18Zh148.
98. Belgian P.619334 (1962); Chem.Abs., 1963, **59**, 11382.
99. BRD P.1167836 (1964); Chem.Abs., 1964, **60**, 1841.
100. A.F.Grapov and N.N.Mel'nikov, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 1984, **26**, 40.
101. G.A.Kutyrev, A.A.Kutyrev, R.G.Islamov, R.A.Cherkasov, and A.N.Pudovik, Dokl.Akad. Nauk SSSR, 1981, **256**, 601.
102. V.Palm, "Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii" (Fundamentals of a Quantitative Theory of Organic Reactions), Izd.Khimiya, Leningrad, 1977, p.106.
103. A.A.Kutyrev, Candidate's Thesis in Chemical Sciences, Kazan State University, Kazan, 1981.
104. L.Melander, Acta Chem.Scand., 1971, **25**, 3821.
105. S.Nagakura, T.Nakajima, and T.Yonezawa, "Introduction to Quantum Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1981, p.260 [Chem.Abs., **98**, 22642m, Russian ref.only (Ed.of Translation)].
106. R.A.Cherkasov, Doctoral Thesis in Chemical Sciences, Kazan State University, Kazan, 1975.
107. G.A.Kutyrev, A.A.Kutyrev, R.A.Cherkasov, and A.N.Pudovik, Phosphorus and Sulfur, 1982, **13**, 135.
108. G.A.Kutyrev, R.G.Islamov, A.V.Lygin, L.M.Yagfarova, R.A.Cherkasov, and A.N.Pudovik, Zhur. Obshch.Khim., 1983, 53, 1005.
109. A.I.Prokof'ev, N.P.Provotorova, N.A.Kardanov, N.N.Bubnov, S.P.Solodovnikov, V.V.Ershov, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1865.
110. F.Ramirez and I.Ugi, Bull.Soc.chim.France, 1974, 453.
111. A.N.Pudovik, I.V.Gur'yanova, and E.A.Ishmaeva, Symposium, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Izd.Khimiya, Moscow, 1968, Vol.19, p.77.
112. J.Kitayama and T.Satoh, J.Chem.Soc.Jap., Chem. and Ind.Chem., 1980, 1309.
113. H.-J.Kallmayer, Arch.Pharm., 1979, **312**, 230.
114. I.O Sutherland, "Comprehensive Organic Chemistry" (Translated into Russian), Izd.Khimiya, Moscow, 1982, Vol.3, p.572.
115. R.H.Thomson and R.D.Worthington, J.Chem.Soc., Perkin Trans.I, 1980, 282.
116. V.Horak and W.B.Mannig, J.Org.Chem., 1979, **44**, 120.
117. S.I.Burmistrov, V.V.Toropin, and K.S.Burmistrov, Vop.Khim.i Khim.Tekhnol.Khar'kov, 1980(61), 36.
118. Japanese P.5731718 (1983); Ref.Zhur.Khim., 1984, 19N136.
119. K.Shudo, Y.Orihara, T.Ohta, and T.Okamoto, J.Amer.Chem.Soc., 1981, **103**, 943.
120. A.N.Pudovik, G.V.Romanov, and A.A.Lapin, Zhur. Obshch.Khim., 1976, **46**, 1409.
121. H.-J.Lang, Diss., Dokt.Naturwiss, Friedrich-Alexander.Univ., Erlangen-Nürnberg, 1969; Ref. Zhur.Khim., 1970, 1Zh503.
122. D.N.Nicolaides and K.E.Litinas, J.Chem.Res. Microfiche, 1983(6–7), 0658.
123. Yu.G.Shermolovich, R.I.Vlyazlo, and L.N.Markovskii, Zhur.Obshch.Khim., 1978, **48**, 539.
124. F.Ramirez, Bull.Soc.chim.France, 1966, 2443.
125. F.Ramirez, H.J.Kugler, and C.P.Smith, Tetrahedron, 1968, **24**, 1931.
126. A.I.Prokof'ev, T.I.Prokof'eva, I.S.Belostotskaya, N.N.Bubnov, S.P.Solodovnikov, V.V.Ershov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, 1979, **246**, 340.

127. N.A.Mukmeneva, V.Kh.Kadyrova, V.V.Moskva, and N.A.Moskva, Zhur.Obshch.Khim., 1985, **55**, 695.
128. M.G.Pavlichenko, B.E.Ivanov, B.I.Pantukh, V.N.Eliseenkov, and F.B.Gershanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 1909.
129. M.M.Sidhy, M.R.H.Mahran, W.M.Abdou, and T.S.Hafez, Egypt.J.Chem., 1984, **27**, 809.
130. A.Alkerti, A.Hudson, G.F.Pedulli, W.G.McGimpsey, and K.S.Wan Jeffrey, Canad.J.Chem., 1985, **63**, 917.
131. B.D.Sviridov, V.I.Porkhun, M.V.Serdobov, Yu.S.Ryabokobylko, G.M.Adalova, and R.V.Poponova, Zhur.Obshch.Khim., 1986, **56**, 1268.
132. S.-O.Lawesson, Bull.Soc.chim.France, 1986(2), 283.
133. A.A.Kutyrev, D.G.Ovrutskii, and V.V.Moskva, Zhur.Obshch.Khim., 1986, **56**, 1185.
134. A.A.Kutyrev, S.G.Fomin, and V.V.Moskva, Zhur. Obshch.Khim., 1986, **56**, 1908.

Kirov Kazan Institute of Chemical Engineering