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# Dismutation of Arylene Phosphorodiamidites: Specific Features and Aspects of Preparative Use

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**Abstract** — The dismutation of arylene phosphorodiamidites derived from the simplest phenols and naphthols and of their dibasic analogs was studied. The main regular trends of this process and the limits of its synthetic applicability were determined.
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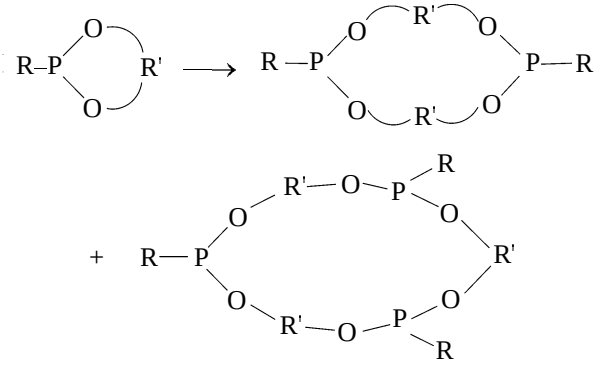
Exchange of substituents at the trivalent phosphorus atom in reactions of two identical molecules (dismutation) is known for a long time. An example is popular synthesis of diphenylchlorophosphine from phenyldichlorophosphine [1]:

$$2PhPCl_2 \longrightarrow Ph_2PCl + PCl_3.$$

This reaction involves the cleavage of strong carbon–phosphorus bond and requires considerable heating. At the same time, in the series of alkylene phosphonites exchange of substituents leading to formation of macrocycles occurs much more readily [2].

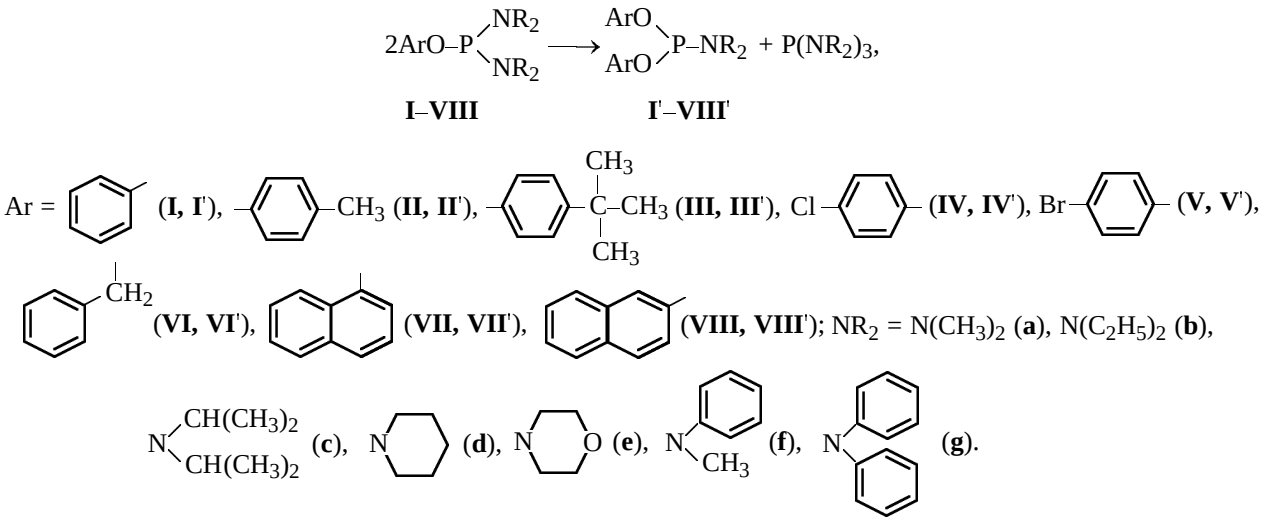


A similar reaction is dismutation of two trivalent phosphorus derivatives having different substituents, e.g., triphenyl phosphite and hexaethylphosphorous triamide [3]. When an equimolar mixture of these compounds is kept for two weeks, a mixture containing $P(OPh)_3$, $(PhO)_2PNEt_2$, $PhOP(NEt_2)_2$, and $P(NEt_2)_3$ in 5 : 7 : 9 : 6 molar ratio is formed. Further keeping of this mixture for up to 8.5 months does not cause further changes in its composition. Similar transformations were noted in the systems $(PhO)_3P$–$PCl_3$ [4] and $PCl_3$–$(NR_2)_3P$ [5]. Comparison of the experimental data shows that the reactivity of P(III) compounds increases in the following series of substituents at the P atom: Ph < PhO < AlkO < $R_2N$ [6]. Furthermore, the exchange rate is influenced by the solvent [7]. Unfortunately, the mechanism of dismutation of trivalent phosphorus derivatives was not discussed in the literature.

In this context, our goals were to reveal the main regular trends in dismutation of the simplest aryl phosphorodiamidites and arylene bis(phosphorodiamidites); to find how the dismutation is influenced by the reactant structures and concentrations, solvent, and catalyst; and to assess the prospects for using aromatic amidophosphites in the design of phosphorus-containing macrocycles.

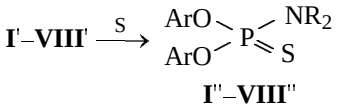
Our studies of dismutation of the simplest aryl phosphorodiamidites have shown that many of aryl phosphorodiamidites in the neat form are stable and do not change during several weeks. At the same time, in solutions they undergo dismutation. In this connection, we first studied the simplest aryl phosphorodiamidites at room temperature.

The reaction progress (see scheme below) was monitored by $^{31}P$ NMR spectroscopy (decrease in the intensity of signals in the range 127–132 ppm characteristic of diamido esters and increase in the intensity of signals at 136–147 ppm typical of amido diesters and also of the signals at 115–122 ppm characteristic of phosphorous triamides). The reaction was considered to be complete (total dismutation) when the signal of the starting diamido ester disappeared from the $^{31}P$ NMR spectrum of the reaction mixture. Note that in some experiments we have observed only partial exchange of substituents and attainment of an equilib-



rium between the starting diamido esters **I**–**VIII** and amido diesters **I**'–**VIII**'' and triamides formed by the reaction. Such cases have been reported previously [6].

Because isolation of pure amido diesters **I**'–**VIII**' from the reaction mixture was difficult, they were identified by $^{31}$P NMR spectroscopy. In some cases, to confirm their formation, we converted them to the corresponding phosphorothioates (**I**''**c, I**''**e, I**''**f, I**''**g, VI**''**b, VII**''**a, VII**''**f, VIII**''**b**), which were isolated pure by column chromatography and completely characterized.

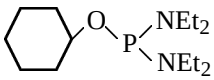


**I**''–**VIII**''

*N*-Alkyl-substituted diaryl phosphoramidites formed in the reaction do not undergo further dismutation in the course of a week even at elevated temperature.

We found that the solvent is one of the factors affecting the dismutation time (Table 1).

Table 1 shows that, with the phenyl esters, transformation of diamido esters I into amido diesters is, as a rule, the fastest in methylene chloride, benzene, and diethyl ether and the slowest in dioxane. Hexane occupies an intermediate position. Phenyl phosphorodimorpholidites **Id** and **Ie** are an exception: Their dismutation is the fastest in dioxane and the slowest in methylene chloride. We believe that this is associated with the structural similarity of 1,4-dioxane and the morpholine fragment of the molecule. In acetonitrile, an equilibrium is often attained. In the case of *p*-substituted phenyl phosphites **II**–**IV**, dismutation is observed only in methylene chloride and dioxane, whereas in all the other solvents virtually no reaction is observed (except **IVb**). This is probably determined by the electronic effects of substituents, i.e., by the shift of the electron density of the benzene ring, which in this case prevents the polarization of the P–O and P–N bonds involved in the reaction. With the chloro and bromo derivatives, the electron density is shifted from the ester oxygen involved in the conjugation with the aromatic ring. This, in turn, apparently affects the $p_\pi$–$d_\pi$ interactions in the amide moiety and enhances the stability of the molecule as a whole. On the other hand, in the case of methyl derivative **IIb** the effect is enhanced by hyperconjugation, leading to the opposite result and ultimately enhancing the $p_\pi$–$d_\pi$ conjugation in the amide moiety. This leads to deactivation of the molecule in the dismutation. Methylene chloride and dioxane most probably exert a directed solvating effect and thus make weaker the effects of conjugation and facilitate the dismutation. In the case of compound **IIIb** containing a bulky substituent in the aromatic ring in the *p*-position relative to oxygen, an important role is played not only by the *+I* effect, but also by the steric factor. As a result, the mutual approach of the molecules is complicated, and virtually no dismutation is observed.



**IX**

We believe that one of the key factors causing the transformation of such a type is the presence of an aromatic fragment in the molecule. Indeed, when the phenyl group in the starting compound is replaced by the cyclohexyl group (compound **IX**), the dismutation is observed neither in the neat state nor in solution, even at elevated temperatures. The possibilty of dismutation of alkyl (Me, *i*-Pr) phosphorodiamidites on heating was shown previously, but in these expe-

**Table 1.** Time (days) required for complete dismutation of compounds **Ia, Ib, Id, Ie, IIb–VIIIb, XIV–XVI**, and **XXXIa–XXXVIa** in various solvents at room temperature

| Comp. no. | $CH_3CN$ | $CH_2Cl_2$ | 1,4-Dioxane | $C_6H_6$ | $(C_2H_5)_2O$ | $C_6H_{14}$ |
|---|---|---|---|---|---|---|
| **Ia** | Equilibrium | 37 | 130 | 60 | 37 | 66 |
| **Ib** | 45 | 48 | 130 | 25 | 40 | 88 |
| **Ic** | 40 | 100 | 39 | 100 | Equilibrium | – |
| **Id** | Equilibrium | 130 | 20 | 56 | ″ | 89 |
| **IIb** | –[a] | 44 | – | – | – | 32 |
| **IIIb** | – | 74 | 27 | – | – | – |
| **IVb** | 90 | 62 | 44 | – | – | – |
| **Vb** | – | – | 18 | – | 35 | – |
| **VIb** | Equilibrium | 200 | Equilibrium | – | Equilibrium | – |
| **VIIb** | ″ | 76 | 175 | Equilibrium | ″ | 150 |
| **VIIIb** | ″ | 68 | 20 | 68 | ″ | 80 |
| **XIVa** | 25 | 32 | 50 | – | – | – |
| **XIVb** | 61 | – | Equilibrium | – | – | – |
| **XVa** | 28 | 42 | ″ | – | – | – |
| **XVb** | 96 | – | ″ | – | – | – |
| **XVIa** | 11 | 15 | 27 | – | – | – |
| **XVIb** | 40 | – | Equilibrium | – | – | – |
| **XXXIa** | 18 | 36 | 63 | Equilibrium | 40 | – |
| **XXXIIa** | 12 | 120 | 51 | 87 | 45 | – |
| **XXXIIIa** | 16 | 30 | 130 | 30 | 70 | – |
| **XXXIVa** | 25 | 40 | 63 | Equilibrium | 40 | – |
| **XXXVa** | 23 | 22 | 70 | 29 | 51 | – |
| **XXXVIa** | 15 | 18 | 80 | Equilibrium | 48 | – |

[a] No dismutation is detected.

riments formation of hydrophosphoryl compounds was observed [8].

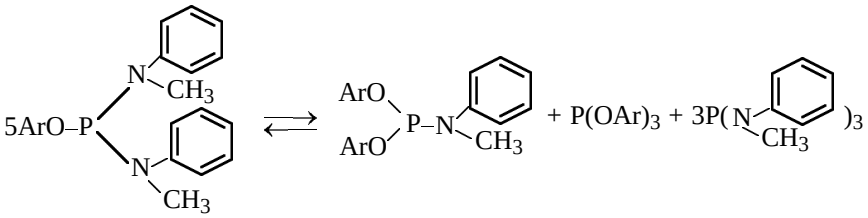
Here we found that the break of the conjugation between the benzene ring and the phosphorus-containing moiety can affect the reaction rate. In particular, benzyl phosphorodiamidites **VIa** and **VIb** undergo extremely slow dismutation in methylene chloride or do not enter the reaction at all.

The dismutation for naphthyl derivatives **VII** and **VIII** is the fastest in methylene chloride and the slowest in hexane. In diethyl ether and in acetonitrile, an equilibrium is attained. β-Naphthyl esters are converted faster than α-naphthyl derivatives. We attribute this fact to different steric arrangement of aromatic fragments relative to the phosphorus-containing moiety.

Examination of effect of the amide substituents on the rate of dismutation of phosphoramidites (Table 1) showed that the reaction was the fastest with the compounds containing aliphatic amide substituents (Me, Et, *i*-Pr), **Ia**–**Ic**. As a rule, the best results were obtained in polar solvents. Derivatives **Id** and **Ie** of heterocyclic amines (piperidine, morpholine) undergo slower dismutation, inrrespective of the structure of the ester moiety.

In the case of phosphoramidites **If** and **VIIIf** containing aromatic amide groups, dismutation evidently occurs along another pathway. The $^{31}P$ NMR spectra recorded in a certain time after the start of the reaction, along the signals of the forming amido diesters at 136 ppm and triamides at 118 ppm, contain also the signal at 130 ppm belonging to triaryl phosphites. Triaryl phosphites are formed only in polar solvents (acetonitrile, methylene chloride) and are not formed in nonpolar and low-polarity solvents (benzene, ether, hexane).

We suggest the occurrence of parallel reactions in this case. Apparently, the rate of elimination of the amide substituent is equal to the rate of elimination of the ester group, which once again confirms the key role of the aromatic system in the dismutation. Thus, this reaction can be described by the following scheme.



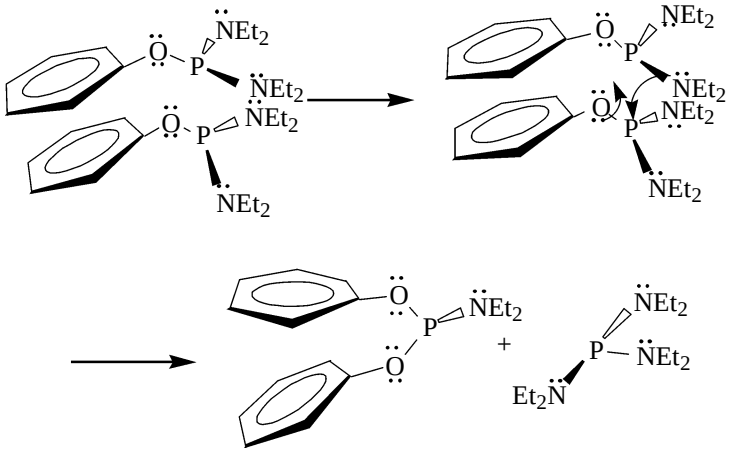
The conversion of the starting amido diester with the given substituents in this reaction is only 20%, and after that an equilbrium is attained. We suggest that this reaction pathway is associated with both electronic and steric factors. Furthermore, the similar equilibrium state in the four-component system was reported previously [3–5].

In this study we examined the effect of the concentration of the starting compounds on the dismutation rate. It is the fastest at the concentration of the starting phosphorodiamidite varied within 1.5–3 M. At higher (>3 M) and lower (<1.5 M) concentrations, the process is slower in all the solvents except methylene chloride in which the trend is opposite (Table 2).

With **Ia, Id**–**Ig, VIb, VIIb, VIIIb**, and **VIIIg**, on reaching the 5 : 1 ratio of $ArOP(NR_2)_2$ and $(ArO)_2 \cdot PNR_2$, an equilibrium is attained, and it is not shifted with increasing temperature. This is attributable to formation of a complex intermolecular associate bound by noncovalent forces. If the equilibrium is not attained and the reactants transform completely, the heating (≤90°C) does not affect the reaction rate either. Apparently, for this reaction room temperature is isokinetic.

We have shown previously[9] that the phenolysis of phosphorustriamides may occur without catalyst (secondary amine hydrochloride), but the rate in this case is much lower. We suggested that this phosphorylation catalyst may also affect the rate of dismutation as the particular case of transphosphorylation. However, actually addition of the catalyst (amine hydrochloride) in any step did not accelerate the reaction.

Taking into account these facts, we suggest the following mechanism of dismutation of aryl tetraalkylphosphorodiamidites. Mutual attraction of two molecules in solution causes the approach of their aromatic fragments. Such associate is held together for some time by the stacking interaction, for which the conditions are the most favorable in monosubstituted phenols. The mutual approach of the aromatic moieties inevitably leads to the approach of phosphorus-containing fragments $-P(NEt_2)_2$.



At a certain time, two such fragnemts may appear in one plane, which will create prerequisites for the redistribution of the electron density with the formation of new bonds leading to the final products. We suggest that one of the key roles in this process belongs to the solvent. It can increase (methylene chloride, 1,4-dioxane) or decrease (benzene, ether) the stacking interaction due to solvation and polarization. Formation of new bonds and alteration of bond angles in the arising diarylene phosphoramidite weaken the stacking interaction, and the aromatic rings are drawn apart.

This scheme also explains why the dismutation of *p*-substituted phenol derivatives is usually complicated and the presence of the aromatic amide component alters the reaction pathway. Apparently, not only the conjugation but also the steric factors influence this reaction.

Dismutation is a second-order reaction, because the reciprocal concentration ($l\ mol^{-1}$) lineary depends on time (days), which was established by substitution of the experimental data in the second-order rate equation $1/c - 1/c_0 = kt$.

To sum up, it can be noted that dismutation of aryl phosphorodiamidites is a complex and multicomponent process which depends on the structural and electronic parameters of substituents at phosphorus, on the polarity and polarizing power of solvents, and also on the concentration parameters.

When studying the phosphorylation of aromatic diols with phosphorous triamides, we noted that at room temperature the arising arylene phosphorodiamidites transform to cyclo(bisarylene phosphoramidites) with the release of phosphorous triamides.

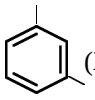
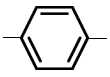
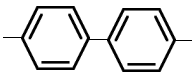
**Table 2.** Time (days) of dismutation of phenyl tetraethylphosphorodiamidite **Ib** in solutions with different molar concentrations

| Solvent | <1.5 M | 1.5–3 M | >3 M |
|---|---|---|---|
| $CH_3CN$ | 90 | 45 | – |
| $CH_2CI_2$ | 29 | 48 | 16 |
| 1,4-Dioxane | 145 | 130 | 190 |
| $C_6H_6$ | 77 | 25 | Equilibrium |
| $(C_2H_5)_2O$ | Equilibrium | 40 | " |

Therefore, the next stage of our study was examining the dismutation of bisphosphorylated dihydric phenols and naphthols. As the aromatic components we initially chose resorcinol **X**, hydroquinone **XI**, and 4,4'-dihydroxybiphenyl **XII**. Hexaethylphosphorous triamide **XIIIa** and phosphorous tripiperidide **XIIIb** were used as phosphorylating agents.

Bisphosphorylation of the above diols was carried out in acetonitrile, methylene chloride, 1,4-dioxane, and diethyl ether at 1 : 2 reactant ratio.

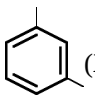
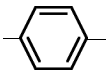
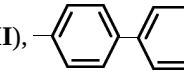
$$\underset{\textbf{X–XII}}{HO–Ar–OH} + 2\underset{\textbf{XIIIa, XIIIb}}{(PNR_2)_3} \longrightarrow \underset{\textbf{XIVa–XVIa, XIVb–XVIb}}{(R_2N)_2PO–Ar–OP(NR_2)_2}$$

Ar =  (**X, XIV**),  (**XI, XV**),  (**XII, XVI**); $NR_2 = NEt_2$ (**a**),  (**b**).

Products **XIV**–**XVI** obtained in the first step of the bisphosphorylation were used without isolation. The reaction progress was monitored by $^{31}P$ NMR spectroscopy. As we showed previously, the rate of bisphosphorylation of diols **X**–**XII** depends on the activity of the leaving group of the phosphorylating agent, on the structure of the diol, and on solvent [10–12].

Keeping of solutions of bisphosphoramidites **XIV**–**XVI** resulted the disappearance of the $^{31}P$ NMR signals of the starting products and accumulation of signals characteristic of monoamido esters and phosphorous triamides. The reaction can be described as follows.

$$\underset{\textbf{XIVa–XVIa, XIVb–XVIb}}{2(R_2N)_2PO–Ar–OP(NR_2)_2} \longrightarrow R_2N–P\begin{matrix}O–Ar–O\\O–Ar–O\end{matrix}P–NR_2 + \underset{\textbf{XVIIa–XIXa, XVIIb–XIXb}}{2P(NR_2)_3},$$

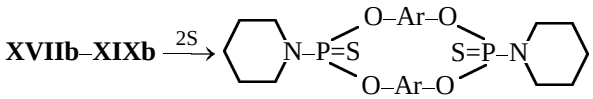
Ar =  (**XIV, XVII**),  (**XV, XVIII**),  (**XVI, XIX**); $NR_2 = NEt_2$ (**a**),  (**b**).

In most cases, the dismutation started when bisphosphorylation was yet incomplete. This fact suggests that the formation of cyclophosphoramidite may be energetically more favorable than the phosphorylation proper.

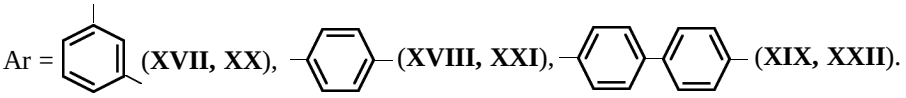
Similarly to the case of the simplest diamido esters, the dismutation rate is mainly governed by the solvent. The transformation of **XIV**–**XVI** into **XVII**–**XIX** is the slowest in 1,4-dioxane and the fastest in methylene chloride. 4,4'-Dihydroxybiphenyl derivatives **XVIa** and **XVIb** are an exception. Their dismutation in 1,4-dioxane is the fastest. Dismutation of hydroqiunone derivatives in diethyl ether and dioxane occurs to only 30–45%, after which the reaction stops. An increase in the temperature of the reaction mixture and in the reagent concentration does not lead to further conversion. Probably, the key role is played by the polarizing and solvating power of the solvent. The times of complete dismutation of **XIV**–**XVI** are given in Table 1.

Table 1 shows that the amide substituent at phosphorus and the aromatic fragment also affect the dismutation time. With the *N*-ethyl substituent at phosphorus, the dismutation time for **XIV**–**XVI** decreases in the order biphenyl > resorcinol > hydroquinone. With the piperidyl substituent, the order is as follows: resorcinol > biphenyl > hydroquinone. This is probably associated with changes in the initial conjugated system which presumably plays an important role in this rearrangement.

It was shown that products **XVIIa**–**XIXa** were completely identical in their physicochemical characteristics to those decribed previously [10–12]. Compounds **XVIIb**–**XIXb** were unknown previously; therefore, the reaction mixture was sulfurized for their complete identification.



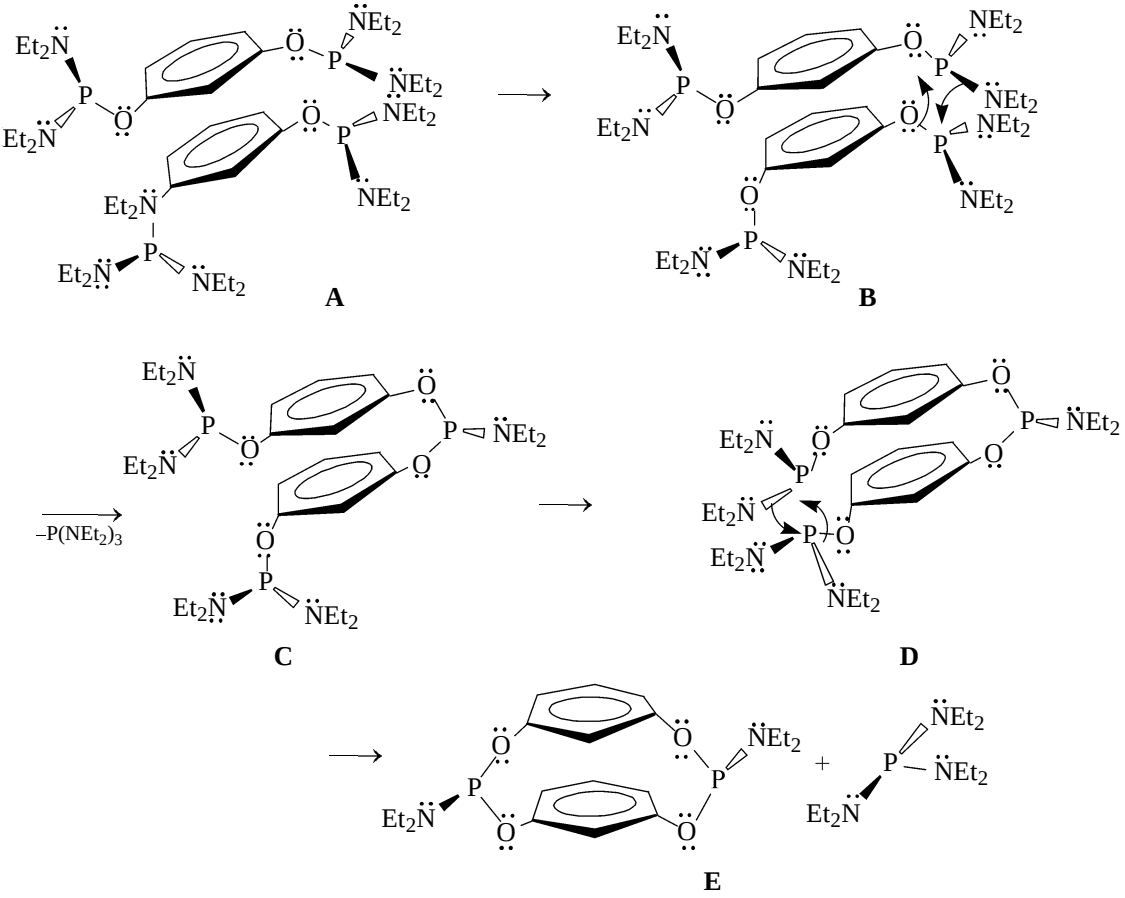

**XXb**–**XXIIb**




Cyclic phosphorothioates **XX**–**XXII** were isolated by column chromatography and completely characterized. Note that hydroquinone derivative **XXIb** strongly decomposes in the column (to approximately 50%), which is presumably associated with the stronger strain of the cyclic system. The physicochemical characteristics of cyclo[bis(*O*,*O*'-*m*-phenylene) bis(phosphoropiperididothioate)] **XXb** completely coincide with those obtained previously [13].

The results obtained suggest that this process is multistep and involves successive rearrangement of two phosphorus centers. Similarly to the simplest aryl phosphorodiamidites **I**–**VIII**, two molecules in solution approach each other under the action of attractive forces and are held together for some time by the stacking interaction to form a molecular associate. The concerted orientation and presence of a common conjugated system should also affect the approach of the interacting molecules. Dismutation of one of the phosphorus-containing fragments follows the previously described scheme.

In diaryl phosphoroamidite **C**, due to the formation of new bonds and changes in the bond angles, the stacking interaction becomes weaker. Then the other phosphoramidite functional groups approach each other, and the process completes with the formation of cyclic system **E**. The scheme suggests that system **C** with one monoamide and two diamide phosphorus centers can exist for a certain time. In this case, addition of sulfur may stop the process at any stage, and the intermediate acyclic products may be isolated. However, sulfurization of the reaction mixture followed by TLC analysis and separation of the reaction products by column chromatography revealed no such product. The $^1$H NMR spectra clearly prove the structure of the sulfurized derivatives of the starting (**A**) and final (**E**) compounds isolated from the reaction mixture. This fact suggests that the rate of dismutation of acyclic product **C** is much higher than the rate of dismutation of bisphosphorylated system **A**. Thus, the limiting step of the process is the dismutation of the starting bis(phosphoramidite). Our experimental data also suggest the possibility of concerted cyclization of

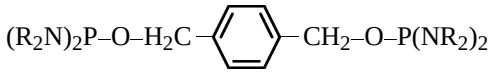


two molecules of bisphosphoramidite, but we believe that such a mechanism is hardly probable.

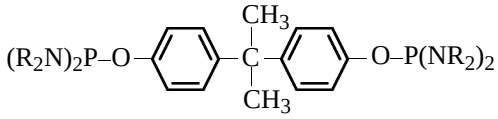
To reveal the effect of acid catalysts on the dismutation rate, we performed a special experiment. Phosphorous triamide **XIIIa** was treated with a butyllithium solution to completely remove amine hydrochloride [14]. Thus treated hexaethylphosphorous triamide was brought into the reaction with resorcinol to form diphosphite **XIVa**, also free of amine hydrochloride. In this case, in contrast to the simplest phosphorous diamido esters, the dismutation time increased by a factor of 1.5 (from 29 to 44 days). Thus, the reaction under study is catalyzed to certain extent by amine hydrochlorides, resembling in this respect the phosphorylation of hydroxy compounds with amides of trivalent phosphorus acids [9].

Increase of temperature does not affect the reaction time.

We found that the **p**–π conjugation leading to formation of a common conjugated system affects the dismutation. For example, bisphosphorylated 1,4-bis(hydroxymethyl)benzene **XXIII** and 2,2-bis(*p*-hydroxyphenyl)propane **XXIV**, as well as benzyl phosphorodiamidites **VI**, do not undergo dismutation. These compounds are stable in polar (acetonitrile, 1,4-dioxane) and nonpolar (ether) solvents.



**XXIII**

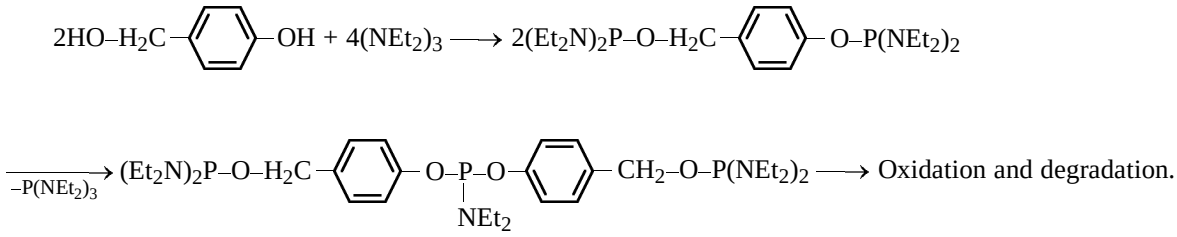


**XXIV**

Compound **XXIII** is characterized by broken conjugation between the aromatic and phosphorus moieties, and compound **XXIV**, by broken conjugation in the aromatic unit and steric hindrance.

It is interesting to examine the dismutation of bisphosphorylated derivatives containing phenyl and benzyl fragments.

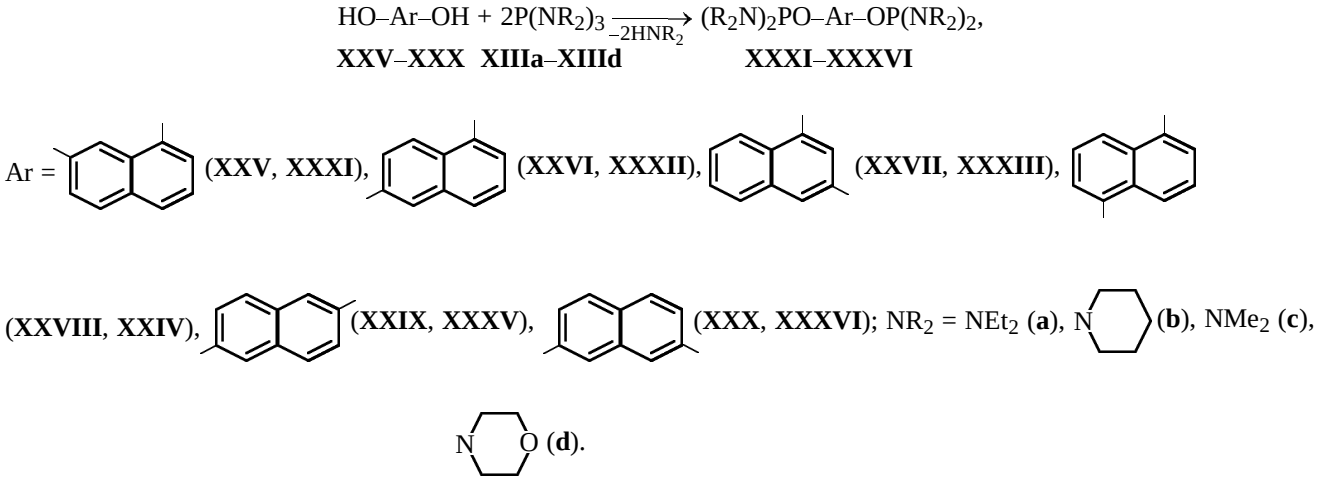
In the first step of bisphosphorylation, 2 h after the start of the reaction, two signals with $\delta_P$ 118 and 132 ppm were observed. They belong to the starting hexaethylphosphorous triamide and aryl phosphorodiamidite, respectively. On the next day, the $^{31}P$ NMR spectrum of the reaction mixture contained two signals with $\delta_P$ 132 and 134 ppm, belonging to bisphos-



phorylated *p*-hydroxybenzyl alcohol, and the signal with $\delta_P$ 118 ppm disappeared. This experiment shows that the benzyl fragment is phosphorylated much more slowly than does the phenyl fragment. After that, on standing of the reaction mixture, the signal at 132 ppm started to disappear, and the signals at 118 and 140 ppm increased in the intensity. The latter two signals belong to the triamide and diaryl phosphoramidite, respectively. This process was complete in 15 days in acetonitrile. The intensity of the signal at $\delta_P$ 134 ppm also started to decrease, with the growth of the signals in the range from –2 to 9 ppm. After storage of the reaction mixture for a month, the $^{31}P$ NMR spectrum contained a signal at 140 ppm and a series of signals in the range 1–9 ppm typical of pentavalent phosphorus. We failed to isolate the reaction product even after the addition of sulfur. Thus, dismutation of compounds of this type involves the phenyl fragments, whereas the benzyl fragments remain intact.

Then, to examine how the dismutation is influenced by the aromatic compoment and the size of the common conjugated system, we performed the dismutation with bisphosphorylated dihydric naphthols with different location of substituents in the ring. Three of them, 1,7-, 1,6-, and 1,3-dihydroxynaphthalenes, are unsymmetrical, and the other isomers, 1,5-, 2,6-, and 2,7-disubstituted compounds, are symmetrical. The presence of a large aromatic core creates good prerequisites for the mutual approach of the molecules in solutions due to stacking interaction [9, 15] and hence should accelerate the dismutation.

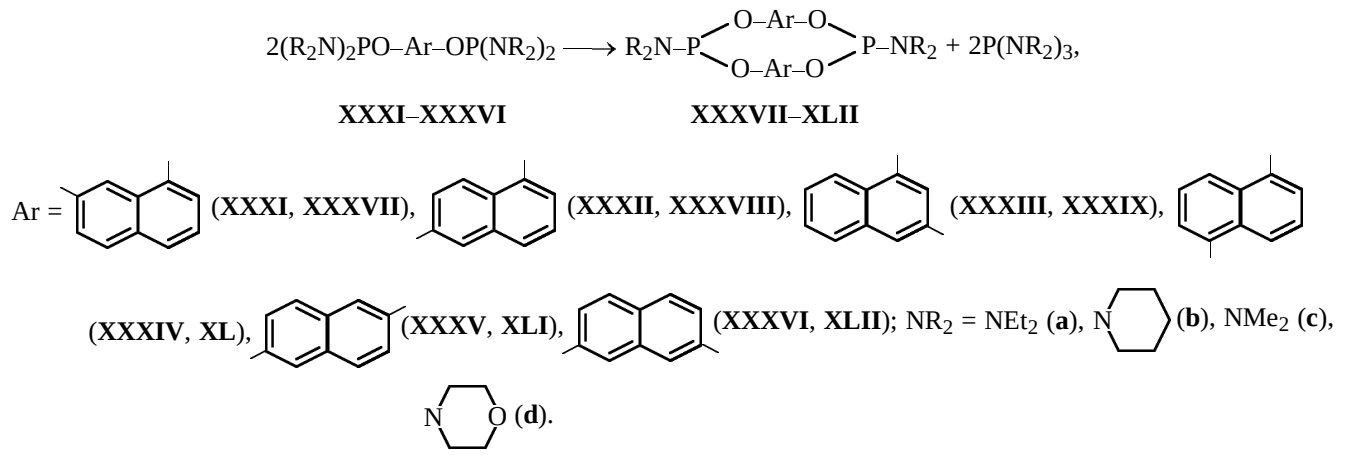
Bisphosphorylation was carried under the conditions similar to those used for dihydric phenols. Along with the above-mentioned phosphorylating agents, we used hexamethylphosphorous triamide **XIIIc** and phosphorous trimorpholide **XIIId**.



Bisphosphorylation of dihydric naphthols in different solvents occurred in different times. The resulting products **XXXI**–**XXXVI**, due to their high reactivity and short lifetime, were previously characterized as phosphorodiamidothioates [16–19]. On standing in solutions, compounds **XXXI**–**XXXVI** start to spontaneously cyclize with the release of phosphorous triamides **XIIIa**–**XIIId**.

The reaction yields cyclo(bisphosphoramidites) **XXXVII**–**XLII**. Their structure and purity were con-

firmed by TLC, $^1H$ and $^{31}P$ NMR spectroscopy, elemental analysis, and molecular weight determination. All physicochemical characteristics were identical to those given in in [16–19].




Cyclo(bisphosphoramidites) **XXXVII**–**XLII** are insoluble in acetonitrile and in the course of dismutation form precipitates, which significantly simplifies their isolation. After the precipitation from the reaction mixture, the morpholine derivatives are practically insoluble in organic solvents, whereas the piperidine derivatives precipitate only from concentrated solutions. The solubility of cyclophosphoramidites depending on the substituent at phosphorus increases in the order morpholino < dimethylamino < diethylamino < piperidino.

Apparently, the dismutation of unsymmetrical bisphosphorylated dihydric naphthols **XXXI**–**XXXIII** can yield two structural isomers with α,β,α,β and α,α,β,β connection of the ester groups.

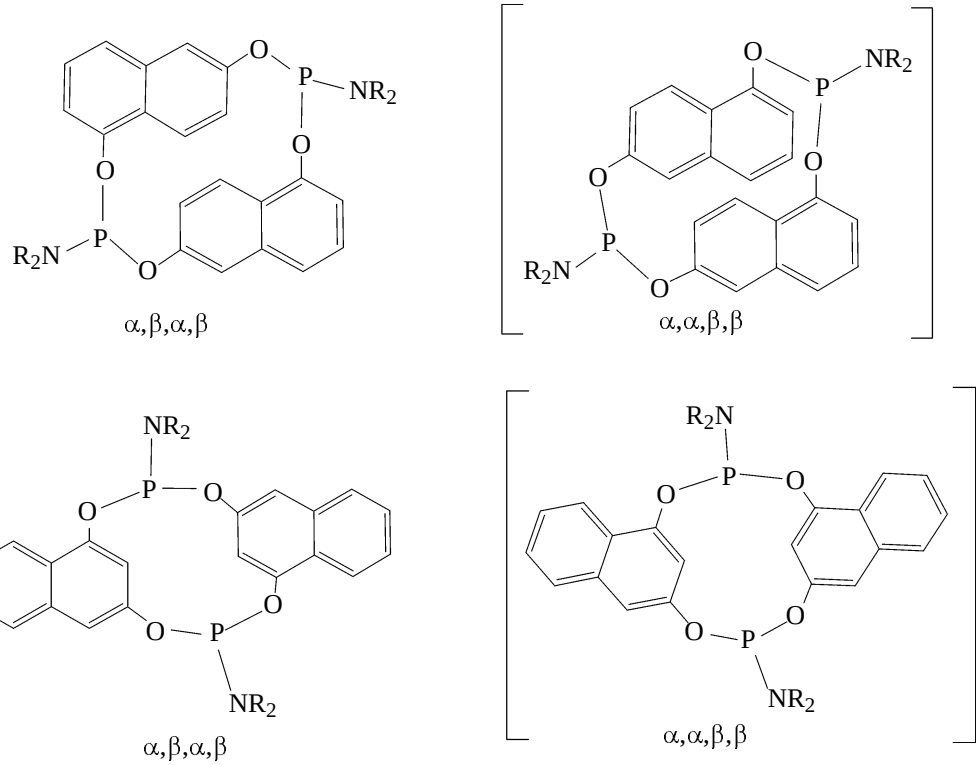


**Table 3.** Steric energies (eV) for **Ib**–**IXb, I'b**–**IX'b, Ia**–**Ig**, and **I'a**–**I'g**

| Comp. no. | $E_{ster}$ | Comp. no. | $E_{ster}$ | Comp. no. | $E_{ster}$ | Comp. no. | $E_{ster}$ |
|---|---|---|---|---|---|---|---|
| **Ib** | 14.0 | **I'b** | 4.1 | **Ia** | 6.9 | **I'a** | 0.4 |
| **IIb** | 14.6 | **II'b** | 11.1 | **Ib** | 13.4 | **I'b** | 10.3 |
| **IIIb** | 18.9 | **III'b** | 15.3 | **Ic** | 26.8 | **I'c** | 5.9 |
| **IVb** | 14.4 | **IV'b** | 10.6 | **Id** | 16.7 | **I'd** | 5.9 |
| **Vb** | 20.6 | **V'b** | 5.9 | **Ie** | 21.1 | **I'e** | 8.5 |
| **VIb** | 18.0 | **VI'b** | 17.7 | **If** | 1.5 | **I'f** | 2.4 |
| **VIIb** | 16.0 | **VII'b** | –6.8 | **Ig** | 3.9 | **I'g** | 2.6 |
| **VIIIb** | 11.3 | **VIII'b** | –6.4 | | | | |
| **IXb** | 25.8 | **IX'b** | 35.6 | | | | |

However, the $^{1}H$, $^{13}C$, and $^{31}P$ NMR data show that only one structural isomer with the α,β,α,β configuration is formed. The same results was previously obtained with bisphosphorylated derivatives of 1,7-dihydroxynaphthalene [17]. In the course of molecular assembly and direct synthesis, both structural isomers (α,β,α,β and α,α,β,β) were obtained, whereas in the course of dismutation only the compound of the α,β,α,β configuration was formed. We believe that this fact is associated with different mechamisms of the cyclophosphorylation and dismutation.

Similarly to the case of the simplest diamido esters and bisphosphorylated mononuclear dihydric phenols, the solvent significantly affects the reaction rate and the yield of the products (Table 1). In polar solvents (acetonitrile, methylene chloride, 1,4-dioxane), the reaction is fast and complete, whereas in nonpolar solvents the dismutation in most cases does not go to completion, and the reaction products undergo oxidation and degradation. The dismutation of **XXXI**–**XXXVI** is the fastest in acetonitrile, whereas with the phenyl derivatives and simplest diamido esters methylene chloride is the most suitable.

A specific feature of the dismutation of bis(tetramethylphosphorodiamidites) **XXXIc**–**XXXVIc** in all the solvents except methylene chloride is that the reaction stops when the cyclophosphite : bisphosphite ratio reaches 1 : 4. Such factors as heating and variation of the concentration of the reaction mixture do not affect the process. Only 2,7-dihydroxynaphthalene derivative **XXXVI** undergoes complete dismutation in all the solvents studied.

The 2,7-dihydroxynaphthalene derivatives undergo the dismutation the most rapidly, and the 1,5-dihydroxynaphthalene derivatives, the most slowly, irrespective of the activity of phosphorus-containing fragment. The experimental data suggest that naphthalene derivatives containing β-hydroxy groups enter the phosphorylation and dismutation much more readily than do the α-naphthol derivatives. It was already noted that such a relationship is characteristic of monohydric naphthols also.

The presence of a catalyst, secondary amine hydrochloride, in phosphorylation of dihydroxynaphthalenes with hexaethylphosphorous triamide **XIIIa** in all the solvents accelerates the phosphorylation and dismutation by a factor of 2 on the average. For example, in the presence of diethylamine hydrochloride, bis(phosphoramidite) derived from 1,6-dihydroxynaphthalene **XXXII** completely transforms into cyclo(phosphoramidite) **XXXVIII** in acetonitrile in 12 days, whereas with the salt-free hexaethylphosphorous triamide the reaction took 25 days. The deviations from the general trend were observed only with 1,3-bis(tetraethyldiaminophosphinyloxy)naphthalene **XXXIII**. In the absence of the salt, the reaction occurred to only 50%, and after that an equilibrium was attained; however, after the addition of the salt the transformation was complete. Such an effect was observed neither in the dismutation of the simplest diamido esters **I**–**VIII** nor with bisphosphorylated dihydric phenols **XIV**–**XVI**. We believe that the amine hydrochloride acts not as a catalyst, but as a reagent.

As shown previously [3, 20], diphenyl diethylphosphoramidite is more stable than phenyl tetraethylphosphorodiamidite. We confirmed this fact in the course of MM2 calculations of the steric energies of these molecules in the gas phase [21]. Also, we performed such calculations for all the compounds we prepared. We found that the steric energies of the groups of diamido esters consisting of compounds **I**–**VIII, XIV**–**XVI**, and **XXXI**–**XXXVI** are higher than those for the groups consisting of **I'**–**VIII'**, **XVII**–**XIX**, and **XXXVII**–**XLII**, respectively. Derivatives **IX**, **XXIII**, and **XXIV** are an exception; with them, the relationship is inverse. This fact explains why the compounds of this type do not undergo dismutation (see above). The calculation results are listed in Tables 3 and 4.

**Table 4.** Steric energies (eV) for **XIVa**–**XVIa, XVIIa**–**XIXa, XXXIa**–**XXXVIa**, and **XXXVIIa**–**XLIIa**

| Comp. no. | $E^1_{ster}$ | Comp. no. | $E^2_{ster}$ | $E^1 - E^2$ |
|---|---|---|---|---|
| **XIVa** | 33.9 | **XVIIa** | 31.4 | 2.5 |
| **XVa** | 42.4 | **XVIIIa** | 39.1 | 3.3 |
| **XVIa** | 29.4 | **XIXa** | 16.3 | 13.1 |
| **XXXIa** | 30.8 | **XXXVIIa** | 17.8 | 13.0 |
| **XXXIIa** | 30.3 | **XXXVIIIa** | 24.8 | 5.5 |
| **XXXIIIa** | 30.2 | **XXXIXa** | 26.6 | 3.6 |
| **XXXIVa** | 45.3 | **XLa** | 32.1 | 13.2 |
| **XXXVa** | 26.4 | **XLIa** | 19.5 | 6.9 |
| **XXXVIa** | 26.4 | **XLIIa** | 19.7 | 6.7 |

Thus, the process under consideration depends on many factors such as the structure of the aromaric fragment, the substituent at phosphorus, the solvent, and the existence of conjugation in the starting compound. It was shown that the derivatives of condensed aromatic systems undergo dismutation faster than their mononuclear analogs. Note that amide derivatives with the aliphatic substituents at nitrogen undergo dismutation more readily that their heterocyclic analogs. The reaction rate was the highest in methylene chloride, irrespective of the aromatic component and substituents at phosphorus. Nonpolar solvents (benzene, diethyl ether), in principle, do not favor dismutation. Temperature does not effect the dismutation time. The catalyst decreases the process time by a factor of 1.5–2 only in the case of bisphosphorylated systems.

The physicochemical and spectral characteristics of the starting diamido esters **I**–**VIII** are listed in Table 5; the characteristics of amido diesters **I**'–**VIII**', in Table 6; and spetral characteristics of thiophosphates **I**''–**VIII**'', in Table 7.

**Table 5.** Yields, boiling points, densitites ρ, $R_f$ values, and $^1$H and $^{31}$P NMR spectra of **I**–**VIII**

| Comp. no. | Yield, % | bp, °C (*p*, mm Hg) | ρ, g cm$^{-3}$ | $R_f$ (system) | $^1$H NMR spectrum ($CDCl_3$) δ, ppm (*J*, Hz) | $^{31}$P NMR spectrum, $\delta_P$, ppm (solvent) |
|---|---|---|---|---|---|---|
| **Ia** | 77 | 78 (1), 127 (10) | 1.1324 | 0.62 (A), 0.90 (B) | 2.47 m (12H, $CH_3$, $^3J_{PH}$ 8.3), 6.81 d (2H, CH, $^3J_{HH}$ 7.0), 7.18 t (3H, CH, $^3J_{HH}$ 7.1) | 134.1 ($Et_2O$), 135.9 ($CH_2Cl_2$) |
| **Ib** | 76 | 90 (1), 149 (10) | 1.1622 | 0.68 (A), 0.93 (B) | 1.08 m (12H, $CH_3$, $^3J_{HH}$ 7.1), 3.02 m (8H, $CH_2$, $^3J_{PH}$ 12.1), 6.9 d (2H, CH, $^3J_{HH}$ 7.0), 7.22 t (3H, CH, $^3J_{HH}$ 7.1) | 131.9 ($Et_2O$), 133.1 ($CH_2Cl_2$) |
| **Id** | 52 | 100 ($10^{-4}$) | 0.865 | 0.64 (A), 0.92 (B) | 1.54 d.d (12H, $CH_2$), 3.08 d (8H, $CH_2$, $^3J_{PH}$ 4.8), 6.73 d (2H, CH, $^3J_{HH}$ 7.0), 6.82 t (1H, CH), 7.09 t (2H, CH, $^3J_{HH}$ 7.0) | 126.7 ($Et_2O$), 127.4 ($CH_3CN$) |
| **Ie** | 88 | 101 ($10^{-4}$) | 0.3005 | 0.47 (A), 0.60 (B) | 3.09 m (8H, $CH_2$, $^3J_{HH}$ 4.4, $^3J_{PH}$ 5.0), 3.59 m (8H, $CH_2$, $^3J_{HH}$ 4.4), 7.01 d (2H, CH, $^3J_{HH}$ 6.6), 7.26 t (3H, CH, $^3J_{HH}$ 7.2) | 127.0 ($C_6H_6$), 128.0 ($CH_2Cl_2$) |
| **If** | 81 | 34[a] | – | – | 2.78 d (6H, $CH_3$), 6.43 d (4H, NCH), 7.07 t (6H, NCH), 6.73 d (4H, OCH), 7.09 t (6H, OCH) | 120.9 ($Et_2O$), 121.5 ($CH_2Cl_2$) |
| **Ig** | 67 | – | – | – | 6.94 t (3H, CHO, $^3J_{HH}$ 7.3), 7.07 d (2H, CHO), 7.13 t (2H, CHO, $^3J_{HH}$ 7.3), 7.17–7.42 m (20H, ArN) | 130.6 ($C_6H_6$), 131.6 ($C_6H_{12}$) |
| **IIb** | 77 | 112 (1), 168 (10) | 1.086 | 0.73 (A) | 1.07 m (12H, $CH_3$, $^3J_{HH}$ 8.3), 2.29 d (3H, $CH_3$, $^4J_{HH}$ 3.1), 3.05 m (8H, $CH_2$, $^3J_{PH}$ 14.7), 6.9 d (2H, CH, $^3J_{HH}$ 7.0), 7.03 m (2H, CH, $^4J_{HH}$ 3.0) | 131.9 ($Et_2O$), 133.0 ($CH_2Cl_2$) |
| **IIIb** | 84 | 159 (1) | 1.094 | 0.69 (A) | 1.02 m (12H, $CH_3$, $^3J_{HH}$ 7.8), 1.36 s (9H, $CH_3$), 3.05 m (8H, $CH_2$, $^3J_{PH}$ 14.6), 6.66 d (2H, CH, $^3J_{HH}$ 7.0), 7.12 d (2H, CH, $^3J_{HH}$ 7.0) | 132.1 ($Et_2O$), 133.7 ($CH_2Cl_2$) |
| **IVb** | 81 | 152 (1) | 0.9101 | 0.80 (A) | 1.04 m (12H, $CH_3$, $^3J_{HH}$ 7.2), 3.19 m (8H, $CH_2$, $^3J_{PH}$ 10.5), 6.93 d (2H, CH, $^3J_{HH}$ 8.8), 7.07 d (2H, CH) | 132.1 ($C_6H_6$) |

**Table 5.** (Contd.)

| Comp. no. | Yield, % | bp, °C (*p*, mm Hg) | ρ, g cm$^{-3}$ | $R_f$ (system) | $^1$H NMR spectrum ($CDCl_3$) δ, ppm (*J*, Hz) | $^{31}$P NMR spectrum, $\delta_P$, ppm (solvent) |
|---|---|---|---|---|---|---|
| **IVd** | 81 | [b] | 1.261 | 0.77 (A), 0.88 (B) | 1.48 d.d (12H, $CH_2$), 3.03 d (8H, $CH_2$, $^3J_{PH}$ 4.8), 6.95 d (2H, CH, $^3J_{HH}$ 8.8), 7.19 d (2H, CH) | 126.9 ($C_6H_6$), 128.3 ($CH_2Cl_2$) |
| **Vb** | 82 | 171 (1) | 1.106 | 0.79 (A) | 1.08 m (12H, $CH_3$, $^3J_{HH}$ 7.2), 3.11 m (8H, $CH_2$, $^3J_{PH}$ 11.1), 6.91 d (2H, CH, $^3J_{HH}$ 8.5), 7.05 d (2H, CH) | 132.2 ($C_6H_6$), 133.1 ($CH_2Cl_2$) |
| **VIb** | 62 | 142–143 (1) | 1.065 | – | 1.09 m (12H, $CH_3$, $^3J_{HH}$ 8.0), 3.11 m (8H, $CH_2$, $^3J_{PH}$ 11.2), 4.61 s (2H, $CH_2$), 7.17 br.m (5H, CH) | 134.7 ($Et_2O$) |
| **VIIb** | 87 | 138–140 ($10^{-3}$) | 1.185 | 0.61 (A) | 1.09 t (12H, $CH_3$, $^3J_{HH}$ 7.4), 3.3 m (8H, $CH_2$, $^3J_{PH}$ 10.1), 7.21 d (1H, $C^2H$, $^3J_{H^2H^3}$ 6.9), 7.4 m (1H, $C^3H$, $^3J_{H^2H^3}$ 6.9), 7.47 t (1H, $C^7H$, $^3J_{H^7H^8}$ 8.1), 7.49 m (1H, $C^6H$), 7.51 d (1H, $C^4H$), 7.87 d (1H, $C^5H$, $^3J_{H^5H^6}$ 8.2), 8.33 d (1H, $C^8H$, $^3J_{H^7H^8}$ 8.1) | 129.7 ($Et_2O$), 130.2 ($CH_2Cl_2$) |
| **VIId** | 85 | [b] | 1.2318 | 0.56 (A) | 1.56 d (12H, $CH_2$, $^3J_{HH}$ 6.0), 3.2 m (8H, $CH_2$, $^3J_{PH}$ 10.0), 7.19 d (1H, $C^2H$, $^3J_{H^2H^3}$ 6.8), 7.36 m (1H, $C^3H$, $^3J_{H^2H^3}$ 6.9), 7.46 t (1H, $C^7H$, $^3JH^7H^8$ 8.5), 7.51 m (1H, $C^6H$), 7.79 d (1H, $C^4H$), 7.87 d (1H, $C^5H$, $^3J_{H^5H^6}$ 8.8), 8.30 d (1H, $C^8H$, $^3J_{H^7H^8}$ 8.5) | 124.9 ($Et_2O$), 125.7 ($CH_2CI_2$) |
| **VIIf** | 69 | 40[a] | 1.213 | 0.55 (A) | 2.77 s (6H, $CH_3$), 6.68 t (6H, CHN, $^3J_{HH}$ 7.7), 7.65 d (4H, CHN, $^3J_{HH}$ 7.7), 7.15 d (1H, $C^2H$, $^3J_{H^2H^3}$ 6.9), 7.31 m (1H, $C^3H$, $^3J_{H^2H^3}$ 6.9), 7.39 t (1H, $C^7H$, $^3J_{H^7H^8}$ 8.4), 7.48 m (1H, $C^6H$), 7.79 d (1H, $C^4H$), 7.80 d (1H, $C^5H$, $^3J_{H^5H^6}$ 8.8), 8.23 d (1H, $C^8H$, $^3J_{H^7H^8}$ 8.3) | 132.5 ($C_6H_6$) |
| **VIIIb** | 81 | 140–142 ($10^{-3}$) | 1.1559 | 0.59 (A), 0.91 (B) | 1.09 t (12H, $CH_3$, $^3J_{HH}$ 7.2), 3.24 m (8H, $CH_2$, $^3J_{PH}$ 9.4), 7.27 d.d (1H, $C^3H$, $^3J_{H^3H^4}$ 8.8, $^4J_{H^1H^3}$ 2.2), 7.34 t (1H, $C^6H$), 7.37 t (1H, $C^7H$), 7.43 s (1H, $C^1H$, $^4J_{H^1H^3}$ 2.2), 7.76 d (1H, $C^4H$, $^3J_{H^3H^4}$ 8.8), 7.80 d (2H, $C^{5,7}H$) | 131.6 ($C_6H_6$), 132.5 ($CH_2CI_2$) |

[a] Melting point. [b] Viscous oil.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 spectrometer (200 and 80 MHz, respectively) against TMS. The $^{31}$P NMR spectra were measured on a Bruker WP-80SY spectrometer (32.4 MHz) against 85% $H_3PO_4$.

Column chromatography was carried out on silica gel L 100/250; TLC analysis was performed on Silufol plates, elution with 5:1 hexane–dioxane (A), 5:1 benzene–dioxane (B), development by iodine vapor and calcination.

All syntheses were carried out in anhydrous solvents under dry nitrogen. The reaction progress was monitored by $^{31}$P NMR spectroscopy.

Aryl phosphorodichloridites were prepared according to [22]; phosphorous triamides, according to [23, 24]; and diamido esters **Ia**–**VIIIa** and **Ib**–**VIIIb**, according to [25].

The physicochemical characteristics of **XIV**, **XVII**, and **XXIV** were reported in [10, 11]; those of **XV**, **XVI**, **XVIII**, and **XIX**, in [12]; those of **XXb**, in [13]; those of **XXIII**, in [26]; those of **XXXI**–**XXXVII**, in [17]; those of **XXXII**, **XXXV**, **XXXVIII**, and **XLI**, in [18]; those of **XXXIV**, **XXXVI**, **XL**, and **XLI**, in [16]; and those of **XXXIII** and **XXXIX**, in [19].

**Table 6.** $R_f$ values and $^{31}P$ NMR spectra of **I'**–**VIII'**

| Comp. no. | $R_f$ (system) | $^{31}P$ NMR spectrum, $\delta_P$, ppm (solvent) |
|---|---|---|
| **I'a** | 0.56 (A), 0.88 (B) | 139.1 ($C_6H_6$), 140.2 ($CH_3CN$) |
| **I'b** | 0.52 (A), 0.89 (B) | 140.8 ($Et_2O$), 141.4 ($CH_2Cl_2$) |
| **I'c** | | 142.3 ($C_6H_6$) |
| **I'd** | 0.57 (A), 0.88 (B) | 136.5 ($C_6H_6$) |
| **I'e** | 0.42 (A), 0.56 (B) | 135.4 ($C_6H_{12}$), 136.5 ($CH_3CN$) |
| **I'f** | – | 134.9 ($C_6H_{12}$), 135.5 ($CH_2Cl_2$) |
| **II'b** | 0.68 (A) | 141.6 ($CH_2Cl_2$) |
| **III'b** | 0.60 (A) | 140.6 ($C_6H_{12}$), 141.0 ($C_4H_8O_2$) |
| **IV'b** | 0.71 (A) | 141.8 ($CH_3CN$) |
| **IV'd** | 0.70 (A), 0.82 (B) | 135.4 ($C_6H_{12}$), 137.3 ($CH_3CN$) |
| **V'b** | 0.71 (A) | 141.3 ($Et_2O$) |
| **VI'b** | – | 147.8 ($CH_3CN$), 148.2 ($CH_2Cl_2$) |
| **VII'b** | 0.53 (A) | 139.9 ($C_6H_6$), 140.9 ($CH_3CN$) |
| **VII'd** | 0.50 (A) | 135.1 ($C_6H_{12}$), 136.4 ($CH_3CN$) |
| **VIII'b** | 0.50 (A), 0.87 (B) | 140.3 ($C_6H_{12}$), 141.3 ($CH_3CN$) |
| **VII'b** | 0.53 (A) | 139.9 ($C_6H_6$), 140.9 ($CH_3CN$) |

**Phosphorodiamidites Ic–Ig, VIc–VIf, VIIc–VIIf, VIIIc–VIIIf, IIb, IId, IVb, IVd, Vb, and Vd** (acid chloride method, general procedure). To a solution of 1 mol of dry amine in 50 ml of anhydrous hexane (or benzene), a solution of 0.25 mol of acid dichloride in 20 ml of anhydrous hexane was added dropwise with vigorous stirring in a flow of an inert gas at 0°C. After the addition was complete, the reaction mixture was allowed to warm up, stirred for an additional 3 h, and left overnight. The resulting solution was filtered through a bed of freshly calcined $Al_2O_3$ of Brockmann grade II (3.5 × 1 cm); the solvent was removed in a vacuum (15 mm Hg), and the residue was dried (60°C, 2 mm Hg).

**Phosphorodiamidites Ia–IXa and Ib–IXb** (amide method, general procedure). A solution of 0.1 mol of appropriate aromatic hydroxy compound was added to 0.3 mol of phosphorous triamide in 20 ml of dry dioxane. The mixture was stirred for 6 h at room temperature and left for 36 h. The resulting diamine, solvent, and excess phosphorous triamide were distilled off in a vacuum (10 mm Hg), and the residue was distilled in a vacuum (1 mm) or passed through a column packed with $Al_2O_3$ and then dried (60°C, 2 mm Hg).

**Dismutation of phosphorodiamidites I–VIII.** Phosphorodiamidite **I**–**VIII**, 0.2 ml, was placed in an ampule for $^{31}P$ NMR measurements, and 1.2–1.5 ml of a dry solvent (acetonitrile, methylene chloride, 1,4-dioxane, benzene, diethyl ether, or hexane) was added. The ampule was sealed, and the $^{31}P$ NMR spectra were recorded at definite intervals. The reaction was considered to be complete when the signal of the starting diamidite disappeared.

**Phosphoramidothioates I''–VIII''.** Sulfur was added to the reaction mixture from the dismutation, containing a mixture of phosphoramidite and triamide, and solution was heated for 40 h at 70°C. Excess sulfur was filtered off, the solvent was removed in a vacuum, and the residue was chromatographed on a column.

**Dismutation of phosphoramidites derived from bisphosphorylated dihydric phenols XIV–XVI.**

**Table 7.** $R_f$ values and NMR spectra of **I''**–**VIII''**

| Comp. no. | $R_f$ (system) | $^1H$ NMR spectrum ($CDCl_3$), $\delta_P$, ppm ($J$, Hz) | $^{31}P$ NMR spectrum, $\delta_P$, ppm (solvent) |
|---|---|---|---|
| **I''d** | 0.70 (A), 0.65 (A) | 1.61 d.d (12H, $CH_2$, $^3J_{HH}$ 6.2), 3.47 d (8H, $CH_2$, $^3J_{PH}$ 11.1), 7.27 d (4H, CH), 7.35 t (6H, CH, $^3J_{HH}$ 6.5) | 65.1 ($CH_2Cl_2$) |
| **I''f** | 0.59 (A) | 2.77 s (3H, $CH_3$), 6.75–7.8 m (15H, ArO) | 66.7 ($CH_2Cl_2$) |
| **I''g** | 0.55 (A) | 6.94 t (4H, CH, $^3J_{HH}$ 7.3), 7.07 t (2H, CH, $^3J_{HH}$ 7.3), 7.13 t (4H, CH, $^3J_{HH}$ 7.3), 7.15–7.4 m (10H, ArN) | 59.6 ($C_6H_6$) |
| **VI''b** | 0.59 (B) | 1.12 t (6H, $CH_3$, $^3J_{HH}$ 7.0), 3.49 m (4H, $CH_2$, $^3J_{PH}$ 9.1), 5.37 d (4H, $CH_2$, $^3J_{HH}$9.4), 7.3 d (4H, CH), 7.38 t (6H, CH) | 76.7 ($CH_2Cl_2$) |
| **VII''f** | 0.43 (A) | 2.73 s (3H, $CH_3$), 6.72–7.74 m (5H, ArN), 7.65–7.81 m (10H, ArO) | 62.5 ($C_6H_6$) |
| **VIII''b** | 0.71 (A) | 1.24 t (6H, $CH_3$, $^3J_{HH}$ 7.2), 3.5 m (4H, $CH_2$, $^3J_{PH}$ 13.8), 7.5–7.85 m (12H, ArO) | 66.7 ($CH_3CN$), 67.4 ($CH_2Cl_2$) |

Compound **XIIIa** or **XIIIb**, 0.04 mmol, was treated with a solution of 0.2 mmol of dihydric phenol **X**–**XII** in 1 ml of acetonitrile, methylene chloride, dioxane, or ether. After the dismutation of **XVb** or **XVIb** was complete, the solvent was removed, the residue was dissolved in 2 ml of methylene chloride, 0.5 mmol of sulfur was added, and the mixture was kept for 40 h at room temperature. After that the reaction mixture was filtered, the solvent was distilled off, and the residue was chromatographed on a column. Cyclic phosphoramidothioates **XXIb** and **XXIIb** were eluted with 1 : 2 benzene–dioxane. The products were dried in a vacuum (1 mm Hg, 70°C) for 2 h.

**Cyclobis(*O,O*'-1,4-phenylene phosphoropiperididothioate) XXIb.** Yield 30%, oil. $R_f$ 0.89 (B), $\delta_P$ 66.6 ppm ($CH_2Cl_2$).

**Cyclobis(*O,O*'-4,4'-biphenylene phosphoropiperididothioate) XXIIb.** Yield 35%, mp 118–120°C, $R_f$ 0.89 (B). $^1$H NMR spectrum, δ, ppm: 1.64 br.t (12H, $CH_2$), 3.49 m (8H, $CH_2$, $^3J_{PH}$ 9.2 Hz), 7.32 d (8H, CH, $^3J_{HH}$ 7.6 Hz), 7.54 d (8H, CH, $^3J_{PH}$ 8.5 Hz), $\delta_P$ 66.8 ppm (1,4-dioxane).

**Dismutation of bisphosphorylated dihydroxynaphthalenes XXXI–XXXVI.** Compound **XIIIa**–**XIIId**, 0.4 mmol, was treated with a solution of 0.2 mmol of dihydroxynaphthalene **XXV**–**XXX** in 1 ml of acetonitrile, methylene chloride, dioxane, benzene, or diethyl ether. When performing the reactions in acetonitrile, cyclic phosphoramidites **XXXVI**–**XLI** separated out as oils, which were washed with acetonitrile and dried in a vacuum (1 mm Hg, 70°C) for 2 h.

**Cyclobis(1,6-naphthylene phosphoropiperididite) XXXVIIIb.** Yield 39%, oil, $R_f$ 0.72 (A). $^1$H NMR spectrum, δ, ppm: 1.53 br.m (12H, $CH_2$), 3.34 t (8H, $CH_2N$, $^3J_{PH}$ 8.3 Hz), 7.11 d (2H, $C^2H$, $^3J_{H^2H^3}$ 7.7 Hz), 7.28 d (2H, $C^7H$, $^3J_{H^7H^8}$ 9.9 Hz), 7.37 t (2H, $C^3H$, $^3J_{H^2H^3}$ 7.7 Hz, $^3J_{H^3H^4}$ 8.8 Hz), 7.45 s (2H, $C^5H$), 8.17 d (2H, $C^4H$, $^3J_{H^3H^4}$ 8.8 Hz), 8.21 d (2H, $C^8H$, $^3J_{H^7H^8}$ 9.9 Hz), $\delta_P$ 135.7 ppm ($C_6H_6$).

**Cyclobis(1,3-naphthylene phosphoropiperididite) XXXIXb.** Yield 41%, mp 101–103°C, $R_f$ 0.70 (A). $^1$H NMR spectrum, δ, ppm: 1.41 br.m (12H, $CH_2$), 3.19 br.t (8H, $CH_2N$, $^3J_{PH}$ 8.2, 7.7 Hz); 7.05 s (2H, $C^2H$), 7.21 br.m (4H, $C^{6,7}H$), 7.37 d (2H, $C^4H$), 7.62 d (2H, $C^5H$), 8.10 d (2H, $C^8H$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 24.7 s (2C, $CH_2$), 26.5 s (4C, $CH_2$), 44.5 d (4C, $CH_2$, $^2J_{PC}$ 23.1 Hz), 108.9 m (2C, $C^{2,2'}H$), 110.2 d (2C, $C^{4,4'}H$), 120.2 s (2C, $C^{9,9'}$), 122.4 s (2C, $C^{5,5'}H$), 124.0 s (2C, $C^{6,6'}H$), 126.8 s (2C, $C^{8,8'}H$), 126.9 s (2C, $C^{7,7'}H$), 134.9 s (2C, $C^{10,10'}$), 150.9 d (2C, $C^{1,1'}O$, $^2J_{PC}$ 7.5 Hz), 151.3 d (2C, $C^{3,3'}O$, $^2J_{PC}$ 8.8 Hz). $\delta_P$ 135.5 ppm ($C_6H_6$). Found, %: C 64.97; H 6.21; N 5.76. $C_{30}H_{32}N_2O_4P_2 \cdot 0.25C_5H_{11}N$. Calculated, %: C 65.93; H 5.90; N 5.13.

**Cyclobis(2,6-naphthylene phosphoropiperididite) XLIb.** Yield 28%, mp 106–108°C, $R_f$ 0.86 (B). $^1$H NMR spectrum, δ, ppm: 1.5 br.d (12H, $CH_2$), 3.29 br.m (8H, $CH_2N$, $^3J_{PH}$ 6.6 Hz), 7.25 d (4H, $C^{3,7}H$, $^3J_{HH}$ 8.8 Hz), 4.45 s (4H, $C^{1,5}H$), 7.66 d (4H, $C^{4,8}H$, $^3J_{HH}$ 8.8 Hz). $\delta_P$ 136.6 ppm ($C_6H_6$). Found, %: C 65.87; H 5.92; N 5.15. $C_{30}H_{32}N_2O_4P$. Calculated, %: C 65.93; H 5.90; N 5.13.

**Cyclobis(2,6-naphthylene phosphoromorpholidite) XLId.** Yield 20%, oil. $^1$H NMR spectrum, δ, ppm: 3.36 br.m (8H, $CH_2N$, $^3J_{PH}$ 5.5, 6.0 Hz), 3.65 br.d (8H, $CH_2O$), 7.24 d (4H, $C^{3,7}H$), 4.45 s (4H, $C^{1,5}H$), 7.68 d (4H, $C^{4,8}H$). $\delta_P$ 135.2 ppm ($CH_2Cl_2$).

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## REFERENCES

1. Brown, M.P. and Silver, H.B., *Ind. Chem.*, 1961, no. 1, p. 24.
2. Scherer, O.J. and Klusmann, P., *Angew. Chem.*, 1969, vol. 81, p. 743.
3. Fluck, E. and Waser J.R. van, *Z. Anorg. Allg. Chem.*, 1961, vol. 307, nos. 3–4, p. 113.
4. Fluck, E., Waser, J.R. van, and Groenweghe, L.C.D., *J. Am. Chem. Soc.*, 1959, vol. 81, no. 20, p. 6363.
5. Waser, J.R. van and Maier, L., *J. Am. Chem. Soc.*, 1964, vol. 86, no. 3, p. 811.
6. Ivanov, B.E. and Zheltukhin, V.F., *Usp. Khim.*, 1970, vol. 39, no. 5, p. 773.
7. Myshkin, A.E. and Evdakov, V.P., *Zh. Obshch. Khim.*, 1968, vol. 38, no. 8, p. 2393.
8. Zwierzak, A. and Koziara, A., *Tetrahedron*, 1967, vol. 23, no. 5, p. 2243.
9. Nifant'ev, E.E., Gratchev, M.K., and Burmistrov, S.Yu., *Chem. Rev.*, 2000, vol. 100, no. 10, p. 3755.
10. Nifant'ev, E.E., Rasadkina, E.N., and Yankovich, I.V., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 11, p. 1812.
11. Nifant'ev, E.E., Rasadkina, E.N., Yankovich, I.V., Vasyanina, L.K., Bel'skii, V.K., and Stash, A.I., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 1, p. 36.

12. Nifant'ev, E.E., Rasadkina, E.N., and Evdokimenkova, Yu.B., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 3, p. 401.
13. Nifant'ev, E.E., Suvorkin, S.V., Rasadkina, E.N., Selyutina, O.V., and Shishin, A.V., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 8, p. 1263.
14. Burmistrov, S.Yu., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1993, p. 16.
15. Hong, V.H., Lee, J.Y., Cho, S.J., Yun, S., and Kim, K.S., *J. Org. Chem.*, 1999, vol. 64, no. 12, p. 5661.
16. Nifant'ev, E.E., Rasadkina, E.N., Evdokimenkova, Yu.B., Vasyanina, L.K., Stash, A.I., and Bel'skii, V.K., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 2, p. 203.
17. Nifant'ev, E.E., Rasadkina, E.N., Evdokimenkova, Y.B., Stash, A.L., Belsky, V.K., and Vasyanina, L.K., *Heteroatom Chem.*, 2003, vol. 14, no. 5, p. 404.
18. Rasadkina, E.N., Slitikov, P.V., Mel'nik, M.S., and Nifant'ev, E.E., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 7, p. 1170.
19. Rasadkina, E.N., Slitikov, P.V., Pechkina, N.P., Vasyanina, L.K., and Nifant'ev, E.E., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 12, p. 2000.
20. Parks, J.R. and Waser, J.R. van, *J. Am. Chem. Soc.*, 1957, vol. 79, no. 18, p. 4890.
21. Allinger, N.L., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 25, p. 8127.
22. Michaelis, A., *Ann. Chem.*, 1903, vol. 326, p. 129.
23. Tolkmith, H., *J. Org. Chem.*, 1958, vol. 23, no. 5, p. 1682.
24. Burgada, R., *Ann. Chem.*, 1963, vol. 8, nos. 5–6, p. 351.
25. Petrov, K.A., Evdakov, V.P., Bilevich, K.A., Radchenko, V.P., and Nifant'ev, E.E., *Zh. Obshch. Khim.*, 1962, vol. 32, no. 5, p. 920.
26. Nifant'ev, E.E., Rasadkina, E.N., Slitikov, P.V., and Stash, A.I., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2005, no. 2, p. 440.