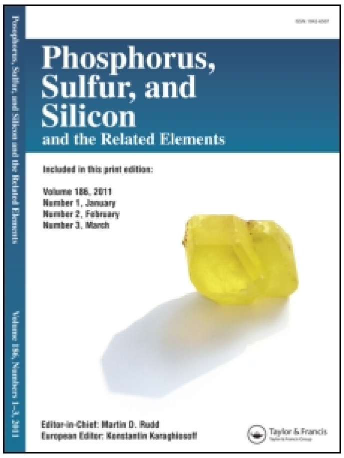

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DISMUTATION OF DIAMIDOARYLPHOSPHITES

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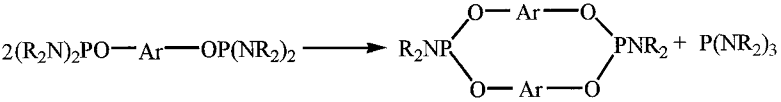
Some examples of spontaneous dismutation of diamidoarylphosphites in different solvents were studied, and features of the process were revealed.

Keywords: Diamidoarylphosphites; dismutation; equilibrium; process features

We studied the phosphorylation of aromatic diols with neutral amides of phosphorous acid and noted a spontaneous transformation of the resulting diamidoarylphosphites to cyclo(bis-amidoarylphosphites) with the release of phosphorous acid triamides at room temperature.[1,2]



SCHEME 1

In fact, this is dismutation, a spontaneous irreversible process, which proceeds without change in the valence of phosphorus.

Transition processes with the participation of identical molecules of trivalent phosphorus derivatives have been known since long ago. They can have unexpected results. Most of them proceed with a change in the coordination of the phosphorus atom[3–5] and require heating, catalyst, or irradiation. The possibility of exchange processes between molecules with similar substituents is noteworthy. In the $P(OPh)_3$–$P(NEt_2)_3$ system, two weeks after the starting reagents were mixed

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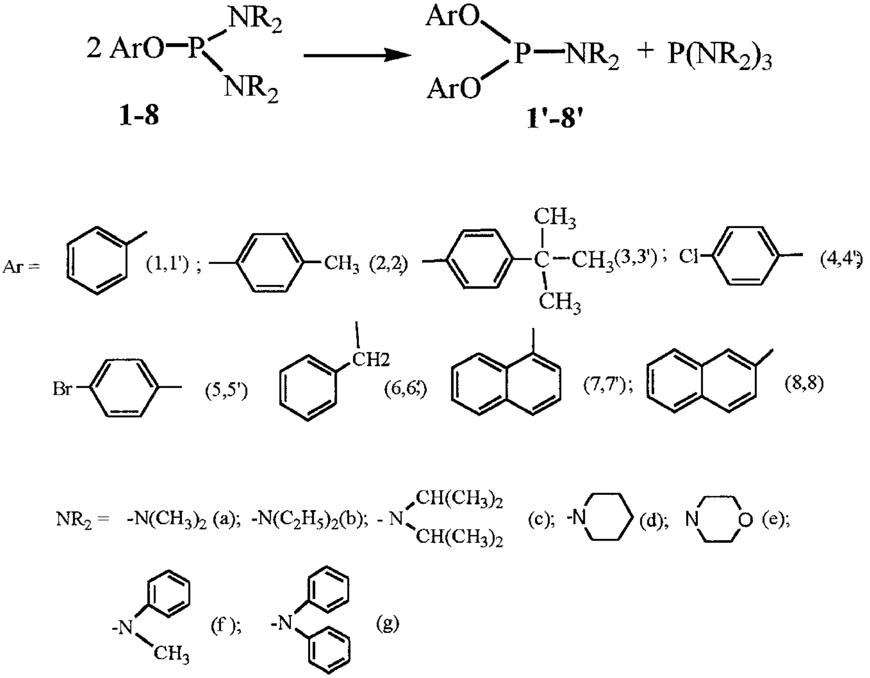
at 25°C, four compounds—$P(OPh)_3$, $PhOP(NEt_2)_2$, $(PhO)_2PNEt_2$, and $P(NEt_2)_3$—were detected by ^{31}P NMR spectroscopy at a molar ratio of 5:7:9:6, which did almost not change for 8.5 months.[6] Thus, spontaneous exchange of acceptor substituents at the trivalent phosphorus atom is a real process. Unfortunately, features of these processes and their motive forces were not discussed in the literature.

RESULTS AND DISCUSSION

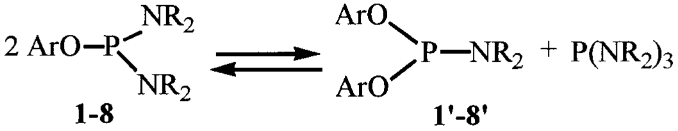
Based on the aforesaid, we began the study of reasons and main features of dismutation with simplest diamidoarylphosphites in order to trace the effects of solvent, reagent concentrations, the structure of aromatic substituent, and the character of amide function in the initial compounds on the process studied. The first stage included the study of behavior of the following diamidoarylphosphites:



SCHEME 2

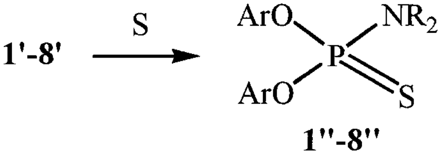
The reaction was performed in solutions at room temperature because it was shown in preliminary experiments that the reaction does not occur in block and that a rise in temperature ($\leq 90°$) has no effect on the rate of the process.

The reaction was monitored with ^{31}P NMR spectroscopy, by the decrease in signal intensities in the range of 127–132 ppm typical for diamidoesters and by the accumulation of signals in the ranges of 136–147 ppm (typical for amidodiesters) and 115–122 ppm (typical for phosphorous triamides). The reaction was considered gone to completion (complete dismutation) when the signal from the initial diamidoester completely disappeared from the ^{31}P NMR spectrum. Note that, in some experiments, we observed only partial exchange of substituents and equilibrium established between the initial diamidoesters (**1–8**) and the resulting amidodiesters (**1′–8′**) and triamides.



SCHEME 3

Amidodiesters **1′–8′** were identified by ^{31}P NMR spectroscopy in the reaction mixture because of isolation problems. However, thionophosphates (**1″c, 1″d, 1″f, 1″g, 6″b, 7″a,f, 8″b**) were obtained in some cases, which were isolated by column chromatography and characterized.



SCHEME 4

It also should be noted that the resulting diarylamidoalkylphosphites **1′–8′** are not subjected to further dismutation.

It is important that the nature of solvent is a factor that can be used for the regulation of dismutation rate (Tables I and II).

For phenyl derivatives, it was noted that the highest transition rate of diamidoesters **1** to monoamidodiesters **1′** is observed in methylene chloride, benzene, and diethyl ether; the lowest rate is observed in 1,4-dioxane. An exception is provided by dipiperidyl and dimorpholidophenyl phosphites **1d** and **1e**, whose dismutation rate is maximal in dioxane and minimal in methylene chloride. We believe that this is related to the structural correspondence of 1,4-dioxane with the

TABLE I The Complete Dismutation Time of Diethylamidoarylphosphites **1b–8b** in Different Solvents at Room Temperature (days)

No.	CH_3CN	CH_2Cl_2	1,4-Dioxane	C_6H_6	$(C_2H_5)_2O$	C_6H_{14}
1b	45	48	130	25	40	88
2b	—[a]	44	—	—	—	32
3b	—	74	27	—	Equilibrium	—
4b	90	62	44	—	—	—
5b	—	—	18	—	35	—
6b	Equilibrium[b]	180	Equilibrium	23	Equilibrium	—
7b	Equilibrium	76	175	Equilibrium	Equilibrium	150
8b	Equilibrium	68	20	68	Equilibrium	80

[a] No dismutation is observed.

[b] Equilibrium is a stable state of the system established at a specific reagent ratio (usually, diesteroamidophosphite:esterodiamidophosphite = 1:4).

piperidyl and morpholine fragments of the molecule. In the case of para-substituted phenyl phosphites **2–5**, dismutation is observed only in methylene chloride and dioxane; it does not occur in other solvents (except for **4b**). This is probably determined by the effect of substituents, i.e., by the shift of electron density on the benzene ring, which hampers the polarization of the "working" P—O and P—N bonds in this case. In chloro and bromo derivatives **4b** and **5b**, the electron density is pulled away from the ester oxygen included in the conjugation of the aromatic fragment, which in turn affects the p_π-d_π interactions in the amide fragment and its stability. In the methyl derivative **2b**, the effect is enhanced by hyperconjugation, which leads to an opposite result in the aromatic fragment and finally enhances the p_π-d_π conjugation of the amide function. This results in the deactivation of the molecule during dismutation. Methylene chloride and dioxane most probably exert a directed solvating action and thus decrease the conjugation effects and make dismutation most possible. In the case of reagent **3b**, which has a bulky substituent in the para position of the aromatic ring with respect to oxygen, both a strong +J effect and a steric factor are essential. As

TABLE II The Complete Dismutation Time of Phenyldiamidophosphites **1a,b,d,e** in Different Solvents at Room Temperature (days)

No.	CH_3CN	CH_2Cl_2	1,4-Dioxane	C_6H_6	$(C_2H_5)_2O$	C_6H_{14}
1a	Equilibrium	37	130	60	37	66
1b	45	48	130	25	40	88
1d	40	100	39	100	Equilibrium	—
1e	Equilibrium	130	20	56	Equilibrium	89

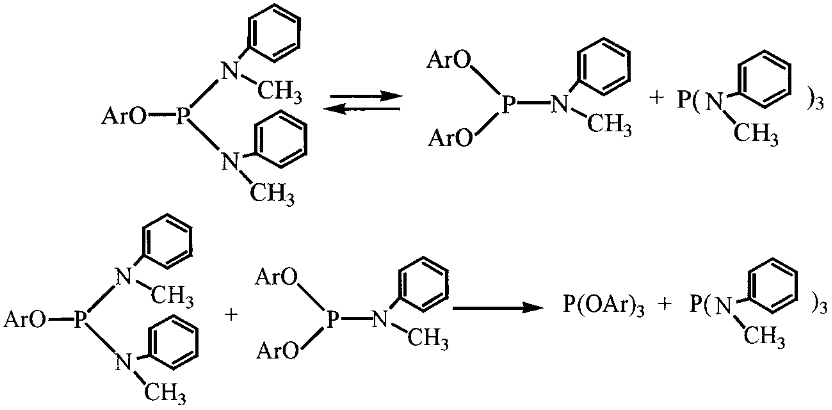
a result, molecules cannot approach each other closely, and almost no dismutation is observed.

For naphthalene derivatives **7** and **8**, the higher transition rate is observed in methylene chloride, and the lowest rate in diethyl ether and acetonitrile (an equilibrium is established). It should be noted that β-naphthol derivatives are dismutated better and more rapidly than α-naphthol derivatives. We attribute this to the different arrangements of aromatic fragments with respect to the phosphorus unit.

It also was interesting to trace how the rupture of conjugation between the benzene ring and the phosphorus unit affects the process rate. For this purpose, we used derivatives **6** with a benzyl radical at the oxygen atom. It was shown that the dismutation of benzyl derivatives, if any, is extremely slow compared to the reagents considered above. The highest rate is attained in methylene chloride, but it decreases in the sequence: phenyl > naphthyl > benzyl.

The study of the effect of amide substituents on the dismutation rate showed that the highest transition rate is observed for compounds with aliphatic amide substituents (methyl, ethyl, and isopropyl) (**1a–c**) and usually in polar solvents. Heterocyclic amides (piperidyl and morpholyl) (**d, e**) are dismutated more slowly, regardless of the ester component.

When reagents containing an aromatic amide component are used, dismutation probably follows another scheme:



SCHEME 5

This direction of the reaction is well observed in ^{31}P NMR spectra. Along with the signals from the resulting diesteroamides, a signal of similar integral intensity appeared in the region of triesters (130 ppm) some time after the beginning of the reaction. The first direction follows the scheme considered above. The second direction, in our opinion,

TABLE III The Dismutation Time (days) of Tetraethyldiamide of Phosphorous Acid Phenyl Ester **1b** as Depending on its Molar Concentration in Different Solvents

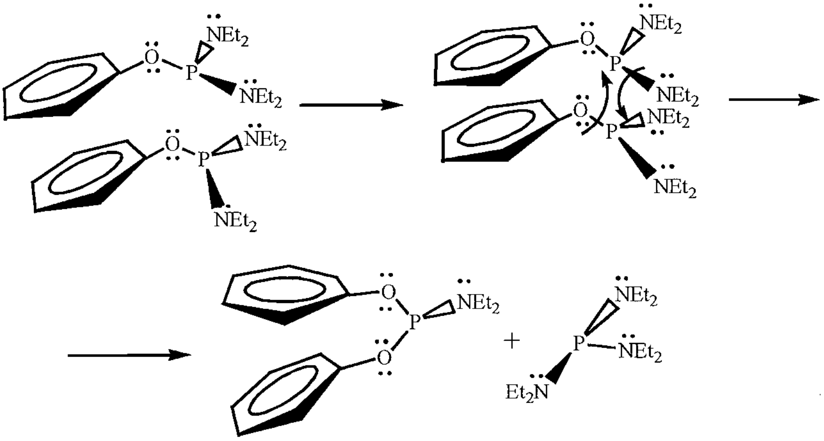
Solvent	<1.5 M	1.5 M–3 M	>3
CH_3CN	90	45	—
CH_2Cl_2	29	48	16
1,4-Dioxane	145	130	190
C_6H_6	77	25	Equilibrium
Et_2O	Equilibrium	40	Equilibrium

includes the interaction between diesteroamide accumulated in the course of reaction and the initial diamidoester. This is probably related to the fact that the ester and amide fragments containing aromatic substituents have similar departure rates. It should be noted that no complete dismutation was observed in this case.

The study of the effect of reagent concentrations showed that the process rate attains maximal values when the initial diamidophosphite concentration is between 0.15 and 3 M. Beyond this concentration range, the dismutation rate decreases in all solvents, except methylene chloride (where the reaction rate increases abruptly (Table III).

We believe that the presence of an aromatic fragment in the molecule is one of the key factors inducing this type of transition. When the phenyl group in the initial compound is substituted by cyclohexyl, no transition is observed either in block, in solution, or under heating.

Based on the foregoing, we suppose the following scheme for the dismutation of dialkylamidoarylphosphites:



SCHEME 6

In solution, two molecules approach each other by aromatic fragments under the effect of attraction and form a molecular associate due to the stacking interaction. It is known that stacking interactions are most frequent in monosubstituted phenols.[7] The approach of aromatic fragments entails an approach of phosphorus units, i.e., of amide fragments. At some time, two of these fragments can be arranged in the same plane, which creates conditions for the redistribution of electron density to form new bonds and, hence, reaction products. It should be noted that stacking interaction plays a part in the initial approach of molecules. Solvent is also essential for this process. It is capable to enhance (methylene chloride and 1,4-dixane) or weaken the stacking interaction due to solvation and polarization. However, stacking interaction in the resulting diarylamidophosphite is weakened because of its low energy (0–50 kJ/mol),[7] and aromatic nuclei are separated.

Stacking interaction can also be responsible for the effect of reagent concentrations on the process rate. The formation of an associate, which can be considered as an important factor of the process, requires an optimal distribution of substance molecules among the solvent molecules. Thus, an increase in the concentration of the initial diamidoester decreases the possibility of its complete solvation. On the other hand, when the diamidoester concentration decreases significantly, the distance between its molecules increases and molecular associates cannot be formed.

In these terms, it is clear that the dismutation of para-substituted phenols is usually hampered and the presence of an aromatic amide fragment changes the process pathway. It is evident that, along with the conjugation effects, steric factors also contribute.

As was shown previously in the literature,[6] diphenyldiethylamidophosphite is more stable than tetraethyldiamidophenylphosphite. We confirmed this fact during the optimization of the geometry of these molecules and the computations of their steric energies in the gas phase using the MM2 program.[8] We also performed similar computations for all synthesized compounds and showed that the steric effects for compounds **1–8** are higher than those for compounds **1′–8′** . An exception is provided by cyclohexyl derivatives (**9**), for which an opposite situation is observed. Therefore, no dismutation occurs for these compounds, as was noted above. Results of calculations are given in Table IV.

On generalizing the results obtained, it can be noted that the dismutation of diamidoarylphosphites is a complex multicomponent process, which depends on the structural and electron parameters of substituents at the phosphorus atom, polarity and polarizing capacity of solvents, and concentration parameters. The study of the process continues, and we would attract attention of colleagues, because many of us

TABLE IV Calculated Steric Energies for Compounds **1b–9b, 1′b–9′b, 1a–f, 1′a–f**

No.	E steric, kcal/mol	No.	E steric, kcal/mol	No.	E steric, kcal/mol	No.	E steric, kcal/mol
1b	12.7	**1″b**	4.0	**1a**	7.2	**1′a**	0.82
2b	14.6	**2″b**	11.0	**1b**	12.7	**1′b**	4.0
3b	18.9	**3″b**	15.3	**1c**	26.8	**1′c**	14.2
4b	14.4	**4′b**	10.6	**1d**	16.7	**1′d**	12.9
5b	20.6	**5′b**	5.9	**1e**	21.0	**1′e**	14.9
6b	18.0	**6′b**	7.4	**1f**	4.6	**1′f**	3.4
7b	16.0	**7′b**	−6.8				
8b	11.3	**8′b**	−6.4				
9b	25.8	**9′b**	35.6				

work with similar unsymmetrical systems capable to dismutate under specific conditions.

EXPERIMENTAL

All syntheses were conducted in dry solvents under a dry nitrogen atmosphere. Reactions were monitored by ^{31}P NMR spectroscopy.

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 (200 MHz). ^{31}P NMR spectra were recorded on a Bruker WP-80SY (32.4 MHz) against 85% H_3PO_4.

Column adsorption chromatography was operated on silica gel L 100/250; TLC was performed on Silufol plates using (A) hexane:dioxane (5:1) and (B) benzene:dioxane (5:1) systems as eluents. Detection was achieved using iodine vapor treatment and calcination. Reaction solutions were filtered through freshly calcinated alumina according to the Brockman II procedure ($d = 3.5$ cm; $h = 1$ cm).

Dichloroanhydrides of phosphorous acid aryl esters were synthesized by the peocedure, introduced by Tolkmith[9] neutral amides were synthesized by the method, introduced by Michaelis[10] phosphorous acid diamidoesters **1–8** (**a,b**) were synthesized by the method introduced by Petrov et al. and Bloshin et al.[11,12]

Diamidoarylphosphites

Amide Method (General Procedure) (1–8 a,b)

The initial aromatic alcohol (0.1 mmol) in 20 ml of dry dioxane was added to 0.3 mmol of phosphorous triamide. The mixture was stirred at room temperature and left to stand for 36 h. The resulting diamine, solvent, and excess of the initial triamide were removed in vacuo; the

TABLE V Physicochemical and Spectral Parameters of Diamidoarylphosphites (**1–8**)

Compound no.	Yield (%)	m.p. (°C) (mm Hg)	Density (g/cm^3)	R_f (eluent)	^{1}H-NMR, (CDCl$_3$), δ (ppm), J(Hz)	^{31}P-NMR, δ, ppm. (solvent)
1a	77	78 (1), 127(10)	1.1324	0.62 (A), 0.9 (B)	2.47 m (12H, CH$_3$, ^{3}J$_{HH}$ 8.34), 6.81 d (2H, CH, ^{3}J$_{HH}$ 7.04), 7.18 t (3H, CH, ^{3}J$_{HH}$ 7.14)	134.14 (Et$_2$O), 135.86 (CH$_2$Cl$_2$)
1d	52	100(10^{-4})	0.865	0.64 (A), 0.92 (B)	1.54 dd (12H, CH$_2$), 3.08 d (8H, CH$_2$, ^{3}J$_{PH}$ 4.76), 6.73 d (2H, CH, ^{3}J$_{HH}$ 6.95), 6.82 t (1H, CH), 7.09 t (2H, CH, ^{3}J$_{HH}$ 6.89)	126.68 (Et$_2$O), 127.43 (CH$_3$CN)
1e	88	101 (10^{-4})	0.3005	0.47 (A), 0.6 (B)	3.09 m (8H, CH$_2$, ^{3}J$_{HH}$ 4.4, ^{3}J$_{PH}$ 4.95), 3.59 m (8H, CH$_2$, ^{3}J$_{HH}$ 4.4), 7.01 d(2H, CH, ^{3}J$_{HH}$ 6.59), 7.26 t (3H, CH, ^{3}J$_{HH}$ 7.15)	127.02 (C$_6$H$_6$), 128.02 (CH$_2$Cl$_2$)
1f	81	34 (melting)	—	—	2.78 s (6H, CH$_3$), 6.43 d (4H, Ar—N), 7.07 t (6H, Ar—N), 6.73 d (4H, Ar—O), 7.09 t (6H, Ar—O)	120.99 (Et$_2$O), 121.51 (CH$_2$Cl$_2$)
1g	67	—	—	—	6.94 t (3H, Ar—O, ^{3}J$_{HH}$ 7.32), 7.07 d (2H, Ar—O), 7.13 t (2H, Ar—O, ^{3}J$_{HH}$ 7.33), 7.17–7.42 m (20H, Ar—N)	130.55 (C$_6$H$_6$), 131.55 (C$_6$H$_{12}$)
2b	77	112 (1), 168 (10)	1.086	0.73 (A)	1.07 m (12H, CH$_3$, ^{3}J$_{HH}$ 8.33), 2.29 d (3H, CH$_3$, ^{4}J$_{HH}$ 3.12), 3.05 m (8H, CH$_2$, ^{3}J$_{PH}$ 14.71), 6.9 d (2H, CH, ^{3}J$_{HH}$ 7.04), 7.03 m (2H, CH, ^{4}J$_{HH}$ 3.02)	131.91 (Et$_2$O), 133.03 (CH$_2$Cl$_2$)
3b	84	159 (1)	1.094	0.69 (A)	1.02 m (12H, CH$_3$, ^{3}J$_{HH}$ 7.78), 1.36 s (9H, CH$_3$—C), 3.05 m (8H, CH$_2$, ^{3}J$_{PH}$ 14.61), 6.66 d (2H, CH, ^{3}J$_{HH}$ 6.97), 7.12 d (2H, CH, ^{3}J$_{HH}$ 6.97)	132.09 (Et$_2$O), 133.67 (CH$_2$Cl$_2$)
4b	81	152 (1)	0.9101	0.8 (A)	1.04 m (12H, CH$_3$, ^{3}J$_{HH}$ 7.15), 3.19 m (8H, CH$_2$, ^{3}J$_{PH}$ 10.45), 6.93 d (2H, CH, ^{3}J$_{HH}$ 8.8), 7.07 d (2H, CH)	132.08 (C$_6$H$_6$)
4d	81	thick oil	1.261	0.77 (A), 0.88 (B)	1.48 dd (12H, CH$_2$), 3.03 d (8H, CH$_2$, ^{3}J$_{PH}$ 4.76), 6.95 d (2H, CH, ^{3}J$_{HH}$ 8.8), 7.19 d (2H, CH)	126.87 (C$_6$H$_6$), 128.33 (CH$_2$Cl$_2$)
5b	82	171 (1)	1.106	0.79 (A)	1.08 m (12H, CH$_3$, ^{3}J$_{HH}$ 7.18), 3.11 m (8H, CH$_2$, ^{3}J$_{PH}$ 11.08), 6.91 d (2H, CH, ^{3}J$_{HH}$ 8.45), 7.05 d (2H, CH)	132.16 (C$_6$H$_6$), 133.12 (CH$_2$Cl$_2$)

(Continued on next page)

TABLE V Physicochemical and Spectral Parameters of Diamidoarylphosphites (**1–8**) *(Continued)*

Compound no.	Yield (%)	m.p. (°C) (mm Hg)	Density (g/cm^3)	R_f (eluent)	^{1}H-NMR, (CDCl$_3$), δ (ppm), J(Hz)	^{31}P-NMR, δ, ppm. (solvent)
6b	62	142–143 (1)	1.065	—	1.09 m (12H, CH$_3$, $^3J_{HH}$ 8.02), 3.11 m (8H, CH$_2$, $^3J_{PH}$ 11.19), 4.61 s (2H, CH$_2$), 7.17 m b (5H, CH)	134.82 (CH$_3$CN), 135.66 (Et$_2$O)
7b	87	138–140 (10^{-3})	1.185	0.61 (A)	1.09 t (12H, CH$_3$, $^3J_{HH}$ 7.41), 3.3 m (8H, CH$_2$, $^3J_{PH}$ 10.12), 7.21 d (1H, CH^2, $^3J_{H}{}^2{}_{\text{-}H}{}^3$ 6.9), 7.4 m (1H, CH^3, $J_{H}{}^2{}_{\text{-}H}{}^3$ 6.9), 7.47 t (1H, CH^7, $^3J_{II}{}^7{}_{H}{}^8$ 8.1), 7.49 m (1H, CH^6), 7.51 d (1H, CH^4), 7.87 d (1H, CH^5, $^3J_{H^5\text{-}H^6}$ 8.2), 8.33 d (1H, CH^8, $^3J_{H}{}^7{}_{\text{-}H}{}^8$ 8.1)	129.66 (Et$_2$O), 130.23 (CH$_2$Cl$_2$)
7d	85	thick oil	1.2318	0.56 (A)	1.56 d (12H, CH$_2$, $^3J_{HH}$ 6.01), 3.2 m (8H, CH$_2$, $^3J_{PH}$ 10.02), 7.19 d (1H, CH^2, $^3J_{H^2\text{-}H^3}$ 6.78), 7.36 m (1H, CH^3, $^3J_{H}{}^2{}_{\text{-}H}{}^3$ 6.9), 7.46 t (1H, CH^7, $^3J_{H}{}^7{}_{\text{-}H}{}^8$ 8.5), 7.51 m (1H, CH^6), 7.79 d (1H, CH^4), 7.87 d (1H, CH^5, $^3J_{H}{}^5{}_{\text{-}H}{}^6$ 8.8), 8.3 d (1H, CH$_8$, $^3J_{H}{}^7{}_{\text{-}H}{}^8$ 8.5)	124.96 (Et$_2$O), 125.68 (CH$_2$Cl$_2$)
7f	69	40 (melting)	1.213	0.55 (A)	2.77 s (6H, CH$_3$), 6.68 t (6H, N—Ar, $^3J_{HH}$ 7.68), 7.65 d (4H, N—Ar, $^3J_{HH}$ 7.66), 7.15 d (1H, CH^2, $^3J_{H}{}^2{}_{\text{-}H}{}^3$ 6.88), 7.3 m (1H, CH^3, $^3J_{H}{}^2{}_{\text{-}H}{}^3$ 6.93), 7.39 t (1H, CH^7, $^3J_{H}{}^7{}_{\text{-}H}{}^8$ 8.39), 7.48 m (1H, CH^6), 7.72 d (1H, CH^4), 7.8 d (1H, CH^5, $^3J_{H}{}^5{}_{\text{-}H}{}^6$ 8.83), 8.23 d (1H, CH^8, $^3J_{H}{}^7{}_{\text{-}H}{}^8$ 8.33)	132.51 (C$_6$H$_6$)
8b	81	140–142 (10^{-3})	1.1559	0.59 (A), 0.91 (B)	1.09 t (12H, CH$_3$, $^3J_{HH}$ 7.15), 3.24 m (8H, CH^2, $^3J_{PH}$ 9.35), 7.27 dd (1H, CH^3, $^3J_{H}{}^3{}_{\text{-}H}{}^4$ 8.8, $^4J_{H}{}^1{}_{\text{-}H}{}^3$ 2.2), 7.34 t (1H, CH^6), 7.37 t (1H, CH^7), 7.43 d (1H, CH^1, $^4J_{H}{}^1{}_{\text{-}H}{}^3$ 2.19), 7.76 d (1H, CH^4, $^3J_{H}{}^3{}_{\text{-}H}{}^4$ 8.8), 7.8 d (2H, CH^{5,7})	131.64 (C$_6$H$_6$), 132.51 (CH$_2$Cl$_2$)

residue was distilled in vacuo (1 mm Hg) or passed through an Al_2O_3 column and dried (70°C, 2 mm Hg).

Chloroanhydride Method (General Procedure) (1c–g, 6–8c–f, 2, 4, 5b,d)

A solution of 0.25 mmol of dichloroarylphosphite in 20 ml of dry hexane was added to 1 mmol of dry amine in 50 ml of dry hexane (or benzene) under intensive stirring and cooling to 0°C. After the phosphorylating agent was added, cooling was removed and the reaction mixture was stirred for 3 h and left to stand overnight. The resulting solution was filtered through an Al_2O_3 layer; solvent was evaporated in vacuo (15 mm Hg), and the residue was dried (70°C, 2 mm Hg).

Physicochemical and spectral parameters of the initial amidodiarylphosphites phosphorous diamidoesters (**1–8**) are given in Table V.

Dismutation Procedure

Diamidoarylphosphite **1–8** (0.2 ml) was placed in an ampoule, and 1.2–1.5 ml of dry solvent was added. The ampoule was sealed, and ^{31}P NMR spectra were recorded in specified time intervals. The reaction was considered terminated when the signal from the initial diamidoarylphosphite disappeared completely.

Physicochemical and spectral parameters of amidodiarylphosphites (**1′–8′**) are given in Table VI.

TABLE VI Physicochemical and Spectral Parameters of Amidodiarylphosphites (**1′–8′**)

Compound no.	R_f (eluent)	^{31}P-NMR, δ, ppm. (solvent)
1′a	0.56 (A), 0.88 (B)	139.09 (C_6H_6), 140.22 (CH_3CN)
1′b	0.52 (A), 0.89 (B)	140.77 (Et_2O), 141.4 (CH_2Cl_2)
1′c	0.6 (A)	142.31 (C_6H_6)
1′d	0.57 (A), 0.88 (B)	136.46 (C_6H_6)
1′e	0.42 (A), 0.56 (B)	135.42 (C_6H_{12}), 136.45 (CH_3CN)
1′f	—	134.94 (C_6H_{12}), 135.47 (CH_2Cl_2)
2′b	0.68 (A)	141.56 (CH_2Cl_2)
3′b	0.6 (A)	140.58 (C_6H_{12}), 141.01 ($C_4H_8O_2$)
4′b	0.71 (A)	141.79 (CH_3CN)
4′d	0.7 (A), 0.82 (B)	135.35 (C_6H_{12}), 137.31 (CH_3CN)
5′b	0.71 (A)	141.31 (Et_2O)
6′b	—	147.79 (CH_3CN), 148.23 (CH_2Cl_2)
7′b	0.53 (A)	139.9 (C_6H_6), 140.89 (CH_3CN)
7′d	0.5 (A)	135.09 (C_6H_{12}), 136.41 (CH_3CN)
8′b	0.5 (A), 0.87 (B)	140.32 (C_6H_{12}), 141.32 (CH_3CN)

TABLE VII Physicochemical and Spectral Parameters of Amidodiaryltionphosphates (**1″–8″**)

Compound no.	R_f (eluent)	^{1}H-NMR, δ, ppm (J, Hz) ($CDCl_3$)	^{31}P-NMR, δ, ppm. (solvent)
1″d	0.7 (A), 5 0.65 (B)	1.61 m (6H, CH_2, $^3J_{HH}$ 6.21), 3.47 m (4H, CH_2, $^3J_{PH}$ 11.14), 7.27 d (4H, CH), 7.35 t (6H, CH)	65.13 (CH_2Cl_2)
1″f	0.59 (A)	2.77 s (3H, CH_3), 6.75–7.8 m (5H, N—Ar)	61.09 (CH_2Cl_2)
1″g	0.55 (A)	6.94 t (2H, O—Ar, $^3J_{HH}$ 7.32), 7.07 t (4H, O-Ar, $^3J_{HH}$ 7.33), 7.13 d (4H, O-Ar), 7.16–7.4 m (10H, N—Ar)	59.59 (C_6H_6)
6″b	0.59 (A)	1.12 t (6H, CH_3, $^3J_{HH}$ 6.95), 3.49 m (4H, CH_2), 5.37 d (4H, CH_2, $^3J_{HH}$ 9.35), 7.3 d (4H, CH), 7.38 t (6H, CH)	66.68 (CH_2Cl_2)
7″f	0.43 (A)	2.73 s (3H, CH_3), 6.72–7.74 m (5H, N—Ar), 7.65–7.81 m (12H, O-Ar)	62.45 (CH_2Cl_2)
8″b	0.71 (A)	1.24 t (6H, CH_3, $^3J_{HH}$ 7.15), 3.57 m (4H, CH_2, $^3J_{PH}$ 13.75), 7.5–7.85 m (12H, CH)	66.74 (CH_3CN), 67.44 (CH_2Cl_2)

Thionophosphoric Acid Amidodiesters (1″–8″)

The calculated amount of sulfur was added to the reaction mixture of amidodiester and triamide obtained after the dismutation. The reaction mixture was heated at 70°C for 40 h and filtered; solvent was removed in vacuo, and the residue was subjected to column chromatography.

Physicochemical and spectral parameters of thionophosphates (**1″–8″**) are given in Table VII.

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