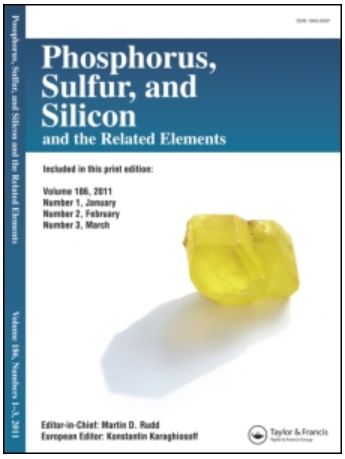


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Dismutation of Bisphosphorylated Aromatic Diols

Edward E. Nifantyev[a]; Elena N. Rasadkina[a]; Pavel V. Slitikov[a]; Larisa K. Vasyanina[a]
[a] Moscow Pedagogical State University, Moscow, Russia

Online publication date: 21 December 2010

To cite this Article Nifantyev, Edward E. , Rasadkina, Elena N. , Slitikov, Pavel V. and Vasyanina, Larisa K.(2005) 'Dismutation of Bisphosphorylated Aromatic Diols', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 2, 513 — 526
To link to this Article: DOI: 10.1080/104265090517244
URL: http://dx.doi.org/10.1080/104265090517244

Phosphorus, Sulfur, and Silicon, 180:513–526, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090517244

Taylor & Francis
Taylor & Francis Group

Dismutation of Bisphosphorylated Aromatic Diols

Edward E. Nifantyev
Elena N. Rasadkina
Pavel V. Slitikov
Larisa K. Vasyanina
Moscow Pedagogical State University, Moscow, Russia

The first study of the dismutation of aromatic diol bisdiamidophosphites has been performed. Derivatives of condensed aromatic systems dismutate more rapidly than their mononuclear analogues. Amide derivatives with aliphatic substituents at the nitrogen atom undergo dismutation more readily than their heterocyclic analogues. In methylene chloride, the process proceeded most rapidly regardless of the aromatic component and the substituent at the phosphorus atom. Apolar solvents (benzene and diethyl ether) did not favor the dismutation. Temperature had no effect on the time of dismutation, and a catalyst decreased it by a factor of 1.5–2.

Keywords Bisphosphorylated aromatic diols; cyclobisaryleneamidophosphites; dismutation; NMR spectroscopy; phosphorous acid triamides

INTRODUCTION

We showed earlier[1] that a spontaneous transformation of simplest phosphorous acid ester diamides into diester monoamides occurs with the formation of phosphorous acid triamide. This process can be defined as dismutation, i.e., an irreversible spontaneous process which proceed without change in the valence of phosphorus. At the same time, we discovered the dismutation of bisphosphorylated aromatic diols.[2–5] These processes result in the formation of a cyclic structure which contains two dihydroxyaryl moieties and two phosphorous acid derivative moieties, and phosphorous acid triamide. These processes are sometimes regioselective.[4,5] It is noteworthy that these reactions do not require any special condition. They proceed in different organic solvents at

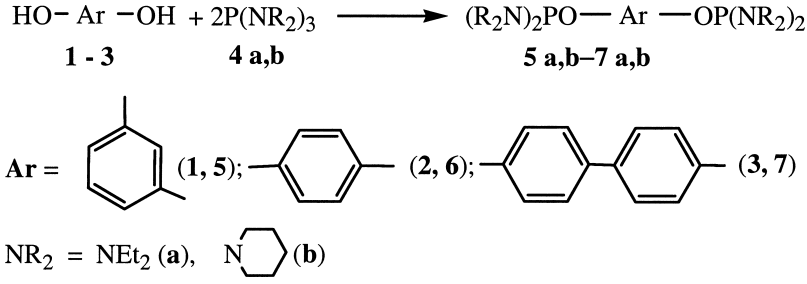
Received June 22, 2004; in final form July 20, 2004.
The work was supported in part by Foundation Russian Universities and the Grant of President of Russian Federation for the State Support of Leading Scientific Schools (NSh-560.2003.3).
Address correspondence to Edward E. Nifantyev, Chemistry Department, Moscow State University, Nesvizky Per. 3, Moscow 119021, Russia. E-mail: chemdept@mtu.net.ru

room temperature with relatively good yield. However, these dismutation processes were not studied in detail.

In this context, we attempted to study the reasons and features of bisdiamidoarylenephosphite dismutation and to monitor the effect of solvent, reagent concentrations, temperature, amine hydrochloride (a known phosphorylation catalyst),[6] the structure of the aromatic substituent, and the amid functions of the initial compounds on the process.

DISMUTATION OF BISPHOSPHORYLATED DIBASIC PHENOLS

At the initial stage of the work, a dibasic phenol—resorcinol (**1**), hydroquinone (**2**) or 4,4′-dihydroxybiphenyl (**3**)—was used as the aromatic component. Phosphorous acid triamides containing acyclic (phosphorous acid hexaethyltriamide) and cyclic (phosphorous acid tripiperidylamide) amide substituents at the phosphorus atom were used as phosphorylating agents. Bisphosphorylation of the above diols was conducted in different solvents (acetonitrile, methylene chloride, 1,4-dioxane, and diethyl ether) at a reagent ratio of 1:2.

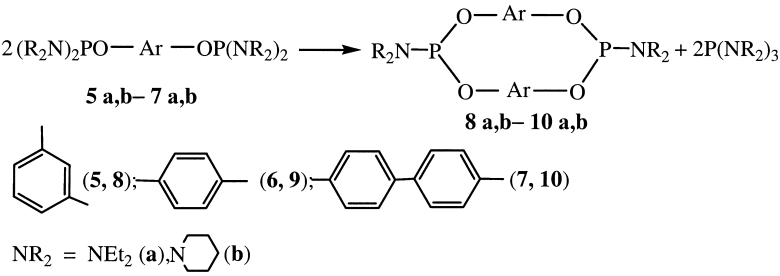


SCHEME 1

Bisphosphorylated products (**5–7**) formed at the first stage were used without isolation. The reaction was monitored by ^{31}P NMR spectroscopy. The advance of the reaction was followed by the disappearance of the triamide signal and the accumulation of phosphorous acid signal at 128–132 ppm. The bisphosphorylation time of diols **1–3** depended on the reactivity of the leaving group of the phosphorylating agent, the nature of the diol, and the solvent used.

When the reaction mixture was left to stand, its ^{31}P NMR spectrum showed the disappearance of signals at 128–132 ppm, as well as the accumulation of signals with a chemical shift of 135–140 ppm typical for phosphorous acid diester monoamides and of a signal due to

phosphorous acid triamides at 115–118 ppm. Taking into account our previous results, the process can be described by Scheme 2.



SCHEME 2

In most cases, dismutation began before the end of bisphosphorylation. This indicates that the formation of cycloamidophosphites (**8–10**) can be energetically more favorable than phosphorylation.

Solvent has the most effect on the time of dismutation. The shortest time of transformation of compounds **5–7** into compounds **8–10** was observed in methylene chloride, and the longest time was observed in 1,4-dioxane. The exception was provided by 4,4′-dihydroxybiphenyl derivatives (**7a**, **b**), for which dismutation proceeded most rapidly in 1,4-dioxane. The dismutation of hydroquinone derivatives in diethyl ether and 1,4-dioxane proceeded only to 30–45% completion, after which the process stopped. The elevation of the reaction mixture temperature and the increase in reagent concentrations had no effect. We believe that the reaction in the solvents led to the formation of stable intermolecular associates of bisphosphorylated products **6** with formed cycloamidophosphites **9**, which brought the system into a quasi-equilibrium state. (Quasi-equilibrium is a stable state of the system in which all three components of the reaction mixture exist simultaneously.) The polarizing and solvating capacity of solvent can play an essential role. Both the initial components (**5–7**) and reaction products (**8–10**) are soluble in methylene chloride, 1,4-dioxane, and diethyl ether. The complete dismutation times of compounds **5–7** are given in Table I.

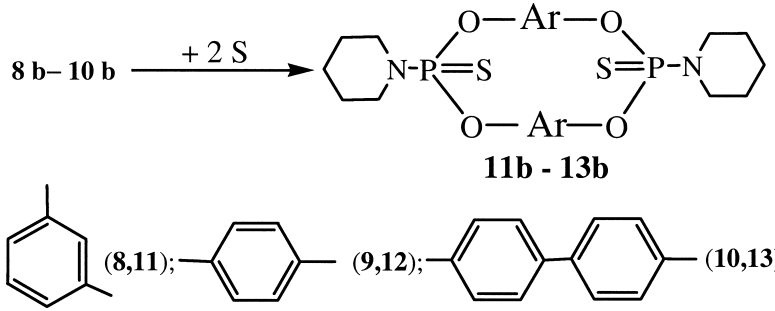
It is seen that *the amide substituent at the phosphorus atom and the aromatic radical* also affect the time of dismutation. In the presence of the *N*-ethyl substituent at the phosphorus atom, aromatic radicals can be arranged by decreasing time spent for the dismutation of their bisphosphorylated derivatives in the following sequence: biphenyl > resorcinol > hydroquinone. In the case of the piperidyl radical, the following sequence is observed: resorcinol > biphenyl > hydroquinone. This can be related to the alteration of the initial conjugated system,

TABLE I Time (Days) of Complete Dismutation for Compounds 5–7 in Different Solvents at Room Temperature

Compound	CH_3CN	CH_2Cl_2	1,4-dioxane
5a	25	32	50
5b	61	—	Quasi-equilibrium
6a	28	42	Quasi-equilibrium
6b	96	—	Quasi-equilibrium
7a	11	15	27
7b	40	—	Quasi-equilibrium

which presumably plays an important role in this rearrangement and the nature of the leaving phosphorus moiety.

It was shown that the physicochemical characteristics of products **8a–10a** correspond to those described in the literature.[3,7,8] Compounds **8b–10b** were obtained for the first time; therefore, the sulfurization of the reaction mixture was performed to identify the obtained cyclic structures in Scheme 3.

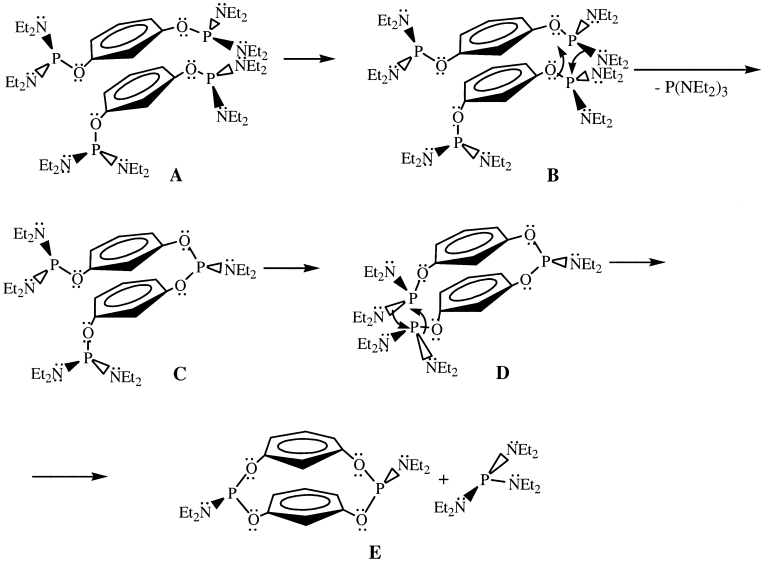


SCHEME 3

The cyclic systems were isolated by column chromatography and characterized as cyclothionophosphates (**11–13**). It is noteworthy that hydroquinone derivative (**12b**) is subjected to a strong destruction on the column (the degree of destruction is about 50%), which is related, in our opinion, to the highly strained structure of the cyclic system. Physicochemical characteristics of cyclo[bis(*m*-phenylenedipiperidylthionophosphate)] (**11b**) coincided with those reported earlier.[9]

From the results obtained, it may be supposed that the described process is multi-staged, i.e., it includes the successive rearrangements of two phosphorus centers.

In solution, two molecules approach each other by aromatic fragments under the effect of attraction forces and are retained together for a time due to stacking interaction by forming a molecular associate. The most efficient stacking interaction is observed for monosubstituted phenols,[10] however, the coordinated orientation and the common conjugated system also should affect the mutual approach of the interacting molecules. The approach of aromatic fragments results in the approach of phosphorus moieties, i.e., of amide fragments. Two such fragments can be arranged in the same plane at a given time, which makes possible the redistribution of electron density with the creation of new bonds and the formation of final products. Stacking interaction plays the determining role in the initial approach of molecules. The solvent is also essential. It can enhance (methylene chloride, 1,4-dioxane) or suppress (benzene, ether) the stacking interaction due to solvation and polarization effects. However, the stacking interaction in the resulting diarylamidophosphite (C), which has a low energy (0–50 kJ/mol,[10] decreases because of the formation of new bonds and the change of valent angles. Then other phosphoamide functions approach each other, and the process is concluded with the formation of a cyclic system E. Scheme 4 shows that a system with one monoamide and two diamide phosphorus centers (C) can exist at a given moment. It follows that an intermediate acyclic product can be isolated when the reaction is stopped at some step by introducing sulfur into the reaction mixture.



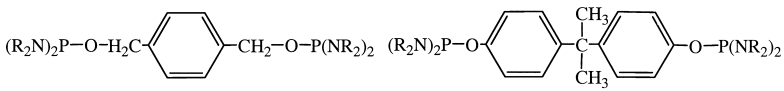
SCHEME 4

Nonetheless, no such product was found when the sulfurized reaction mixture was analyzed by TLC at any step and the reaction products were separated by column chromatography. The structures of initial (A) and final (E) sulfurized compounds isolated from the reaction mixture were unambiguously proved by ^{1}H NMR spectroscopy. This implies that the dismutation rate of acyclic product C is much higher than that of bisphosphorylated system A. Thus, the dismutation of the initial bisamidophosphite is the limiting step of the process. However, the synchronous cyclization of two bisamidophosphite molecules may also be deduced from the experimental findings. In this case, the absence of intermediate acyclic product C is understandable.

The effect of phosphorylation *catalysts* on the dismutation was not considered until now. It was shown previously in our laboratory[6] that the phenolysis of neutral amides is feasible without catalyst (secondary amine hydrochloride), although at a significantly lower rate. To study the effect of acid catalysts on dismutation, the phosphorous acid triamide **4a** was purified from amine hydrochloride by interaction with a butylium solution.[11] The salt-free phosphorous acid hexaethyltriamide was introduced into the reaction with resorcinol. The dismutation time was doubled in this case (from 29 to 44 days). Thus, the introduction of a secondary amine hydrochloride into the reaction solution increases the rate of phosphorylation but decreases the rate of dismutation, which attests to the difference in the mechanisms of these processes.

It was also noted that *the increase in temperature and the change in concentrations of reagents* in a wide range have no significant effect on the process time.

The effect of p-π conjugation, which results in the formation of a unified conjugated system, significantly affects the dismutation of bisphosphorylated systems. So, bisphosphorylated 1,4-bis(hydroxymethyl)benzene (**14**) and 2,2-bis(*p*-hydroxyphenyl)propane (**15**) do not undergo dismutation. These compounds are stable in polar (acetonitrile, 1,4-dioxane) and apolar solvents.

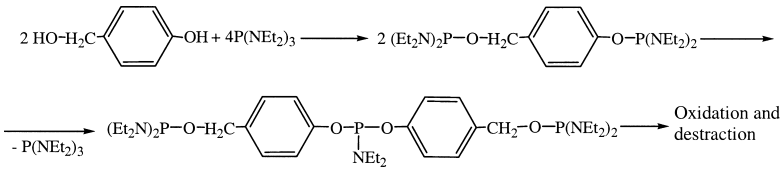


14 **15**

SCHEME 5

Scheme 5 shows that there are disruptions of conjugation between the aromatic and phosphorus moieties of compound **14** and within the aromatic moiety of compound **15**.

Of interest is the dismutation of bisphosphorylated derivatives containing both phenyl and benzyl functions (Scheme 6).



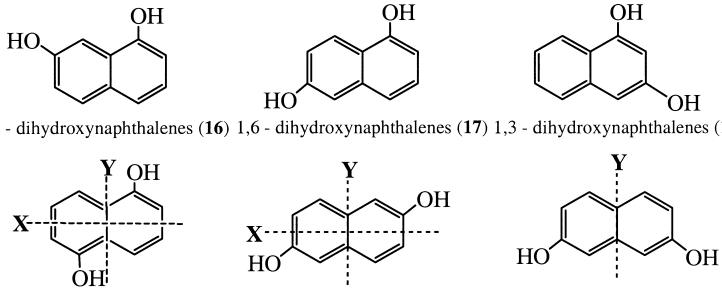
SCHEME 6

At the first bisphosphorylation step, 2 h after the beginning of the reaction, two signals were observed at 118 and 132 ppm in the ^{31}P NMR spectrum of the reaction mixture, which corresponded to the initial phosphorous acid hexaethyltriamide and phosphorous acid diamidoaryl ester, respectively. The benzyl moiety was phosphorylated much more slowly than the phenyl moiety. Two signals with δ 132 and 134 ppm were observed 24 h after the reaction was started, which corresponded to bisphosphorylated *p*-hydroxybenzyl alcohol; the signal at 118 ppm disappeared. As time passed, the signal at 132 ppm disappeared and the signals at 118 and 140 ppm (assigned to the neutral amide and monoamide of phosphorous acid diaryl ester, respectively) accumulated. The process was completed in 15 days in acetonitrile. The signal at 134 ppm also began to decrease, and the signals in the range between −2 and −9 ppm accumulated. After the reaction mixture stood for a month, the signal at 140 ppm remained and some signals appeared in the range from **1–9** ppm, which corresponded to pentavalent phosphorus. The reaction product could not be isolated even after sulfur addition. Thus, the dismutation of these compounds involves only phenyl moieties, and benzyl moieties do not participate in the process.

DISMUTATION OF BISPHOSPHORYLATED DIHYDROXYNAPHTHALENES

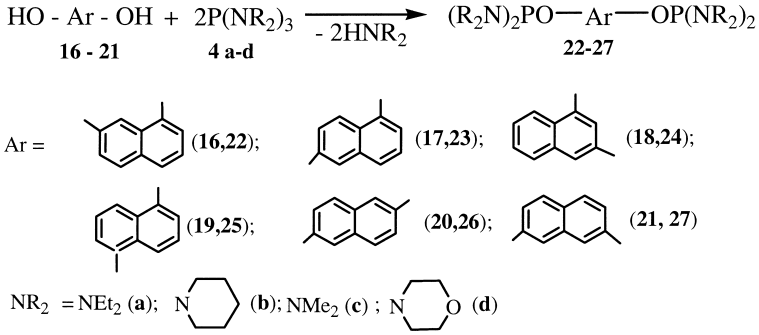
To study the effect of the aromatic component and the size of overall conjugated system on the dismutation process, bisphosphorylated naphthalenediols substituted in different positions of the ring were subjected to dismutation. These were three unsymmetric compounds (1,7-, 1,6-, and 1,3-dihydroxynaphthalenes) and three systems with different symmetry axes (1,5-, 2,6-, and 2,7-dihydroxynaphthalenes).

The powerful aromatic moiety creates good conditions for the mutual approach of molecules in solution due to stacking interaction[10,12] and, hence, for a decrease in dismutation time (Scheme 7).



SCHEME 7

Bisphosphorylation was conducted under the same conditions as for dibasic phenols. Along with the phosphorylated agents mentioned above, hexamethyltriamidophosphite (c) and trimorpholydophosphite (d) were used (Scheme 8).

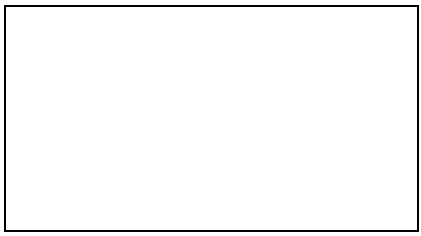


SCHEME 8

The bisphosphorylation of naphthalenediols took different times in different solvents. The obtained compounds (**22–27**) were characterized previously as diamidothionophosphates (because of high reactivity and short lifetime.[2,4,6,13] Upon standing in solution, compounds **22–27** undergo spontaneous cyclization with the formation of phosphorous acid triamide **4a–d** (Scheme 9).

It was shown that the reaction gave cyclobisamidophosphites (**28–33**), which were identified using TLC, ^{1}H and ^{31}P NMR spectroscopy, elemental analysis, and molecular weight determination. All physicochemical characteristics coincided with those reported previously.[2,4,5,13]

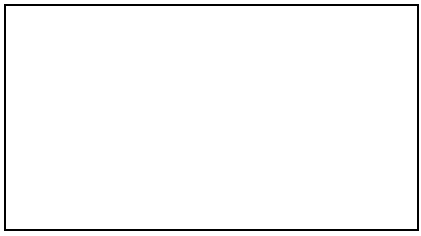
Cyclobisamidophosphites **28–33** are insoluble in acetonitrile; they precipitate during dismutation, which significantly simplifies their isolation. When separated from the reaction mixture, morpholyl



SCHEME 9

derivatives, are hardly soluble in organic solvents and piperidyl derivatives precipitate only from concentrated solutions. The solubility of cycloamidophosphites depends on the substituent at the phosphorus atom and increases in the following sequence of substituents: morpholyl < methyl < ethyl < piperidyl.

The dismutation of unsymmetrical bisphosphorylated naphthalenediols **22–24** can result in the formation of two structural isomers with the successive (α,β,α,β) and pairwise (α,α,β,β) arrangement of hydroxo groups in the cycle (Scheme 10).



SCHEME 10

However, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data showed that only the α,β,α,β-isomer was formed. A similar situation was observed earlier for bisphosphorylated 1,7-dihydroxynaphthalene derivatives. We attribute this to the difference in the mechanisms of cyclophosphorylation and dismutation. In this case, as for mononuclear dibasic phenols, the reaction time and product yields can be regulated by *solvent* selection (Table II).

In diethyl ether and benzene, the reaction is not completed and products undergo oxidation and destruction.

The dismutation of bistetramethyldiamidophosphites **22c–27c** stops at a cyclophosphite-to-bisphosphite ratio of **1**:**4** in all solvents except methylene chloride. The increase in temperature, the change in reagent concentrations, and the addition of catalysts have no effect on the

TABLE II The Time of Complete Dismutation (Days) of Compounds 22a–27a in Different Solvents at Room Temperature

Compound	CH_3CN	CH_2Cl_2	1,4-dioxane	C_6H_6	Et_2O
22a	18	36	63	Quasi-equilibrium	40
23a	12	120	51	87	45
24a	16	30	130	30	70
25a	25	—	63	Quasi-equilibrium	40
26a	23	22	70	29	51
27a	15	18	80	Quasi-equilibrium	48

process. The only exception is provided by 2,7-dihydroxynaphthalene derivative **27**, the dismutation of which is completed in all solvents.

The shortest dismutation time was observed for 2,7-dihydroxynaphthalene derivatives, and the longest time for 1,5-dihydroxynaphthalene derivatives, regardless of the reactivity of the phosphorus center. From the experimental data, it can be inferred that naphthalene derivatives containing β-hydroxy groups enter into phosphorylation and dismutation much more readily than naphthalene derivatives with α-hydroxy groups.

When the phosphorylation of dihydroxynaphthalene with hexaethyltriamides was conducted in the presence of a *catalyst* (secondary amine hydrochloride salt), the dismutation time was approximately halved in all solvents. So, 1,6-dihydroxynaphthalene bisamidophosphite **23** was completely converted into cycloamidophosphite **29** in the presence of diethylamine hydrochloride salt within 12 days; the reaction with salt-free hexaethyltriamide was completed within 25 days. A different situation was observed for 1,3-bis(tetraethyldiamidophosphite)hydroxynaphthalene **24**. In the absence of salt, the reaction proceeded only to 50% completion when quasi-equilibrium was reached; however, after the salt was added, the processes continued to completion.

As was shown earlier,[1,15] monoamides of phosphorous acid diaryl esters are more stable than phosphorous acid ester diamides. This fact was confirmed by our calculation of steric energies for compounds **5a–10a** and **22a–33a** in the gas phase using the MM2 method. We also performed similar calculations for some groups of synthesized compounds and showed that the steric energies calculated for compounds **5–7** and **22–27** are higher than for compounds **8–10** and **28–33**. The results of calculations are presented in Tables III and IV.

The described process depends on many factors: aromatic skeleton, substituent at the phosphorus atom, solvent, and conjugation in the initial molecule (which is the determining factor). Derivatives of

TABLE III Calculated Steric Energies for Compounds 5a–7a and 8a–10a

Compound	$E_{1\,ster.}$	Compound	$E_{2\,ster.}$	E_1–E_2
5	33.96	**8**	31.39	
6	42.44	**9**	39.06	
7	29.39	**10**	16.28	13.11

condensed aromatic systems dismutate more rapidly than their mononuclear analogues. Amide derivatives with aliphatic substituents at the nitrogen atom undergo dismutation more readily than their heterocyclic analogues. In methylene chloride, the process proceeds most rapidly regardless of the aromatic component and the substituent at the phosphorus atom. Apolar solvents (benzene, diethyl ether) do not favor dismutation. Temperature has no effect on the time of dismutation, and catalyst decreases it by a factor of 1.5–2.

EXPERIMENTAL

Syntheses were carried out in dry solvents under a dry nitrogen atmosphere. ^{1}H NMR spectra in $CDCl_3$ (except **32d** in d-DMSO) were recorded on a Bruker AC-200 instrument (200 MHz) with TMS as an internal standard; ^{31}P NMR spectra in acetonitrile, 1,4-dioxane, methylene chloride, benzene, and diethyl ether were recorded on a Bruker WP-80SY at 32.4 MHz (85% H_3PO_4 was used as an external standard). Column chromatography was operated on silica gel L 100/150; thin layer chromatography was conducted on Silufol plates using (a) benzene–dioxane 5:1, (b) benzene–dioxane 1:1, and (c) chloroform–ethanol 5:1 as eluents. The detection of compounds was achieved using calcinations.

Phosphorous acid hexaalkyltriamides were obtained using the reported procedure,[17] as well as tripiperidyl and trimorpholyl phosphites.[18]

TABLE IV Calculated Steric Energies for Compounds 22a–27a and 28a–33a

Compound	$E_{1\,ster.}$	Compound	$E_{1\,ster.}$	E_1–E_2
22	30.8	**28**	17.8	13.0
23	30.3	**29**	24.8	5.5
24	30.2	**30**	26.6	3.6
25	45.3	**31**	32.1	13.2
26	26.4	**32**	19.5	6.9
27	26.4	**33**	19.7	6.7

Physicochemical characteristics of compounds were described earlier: **8a**,[7,8] **9a**, **10a**,[3] **11a**,[9] **22a–c**,[4,18] **25a–c** and **27a–c**,[6,18] **23 a**,**c** and **26a**,**c**.[13]

Dismutation of Compounds 5–7

A solution of 0.2 mmol of phenol **1–3** in 1 mL of acetonitrile, methylene chloride, dioxane, or ether was added to 0.4 mmol of amide **4a**, **b**. Characteristic signals of cycloamidophosphites **8–10** appeared in the ^{31}P NMR spectrum of the reaction mixture (at 140.0–141.3 ppm for ethyl derivatives and at 134.9–135.2 ppm for piperidyl derivatives), as well as signals in the range typical for phosphorous acid triamides formed during the cyclization. The dismutation was considered completed when the signal of phosphorous acid ester diamide (at 128–132 ppm) disappeared and only the signals of diester monoamides (135–140 ppm) and phosphorous acid triamides (115 ppm) remained in the spectrum.

Sulfurization

After the dismutation of compounds **9b**, **10b** was completed, the solvent was distilled from the reaction mixture; the residue was dissolved in 2 mL of methylene chloride and kept with 0.5 mmol sulfur at room temperature for 40 h. Then, the mixture was filtered, solvent was distilled off, and the residue was chromatographed on a column; cycloamidothionophosphates **12b**, **13b** were eluted with the benzene–dioxane (1:2) system. The products were dried at 70°C and 1 mm Hg for 2 h.

Cyclo[bis(1,4-piperidylamidophosphitoxybenzene)] (12b)

Yield 30%.Oily substance. R_f 0.89 (B). ^{31}P NMR (CH_2Cl_2): δ 66.6.

Cyclo[bis(4,4′-piperidylamidophosphitoxybiphenyl)] (13b)

Yield 35%. M.p. 118–120°C. R_f 0.89 (B). ^1H NMR ($CDCl_3$): δ 1.64 t b (12H, CH_2), 3.49 m (8H, CH_2-N, $^3J_{PH}$ 9.2 Hz), 7.32 d (8H, CH, $^3J_{HH}$ 7.6 Hz), 7.54 d (8H, CH, $^3J_{HH}$ 8.5 Hz). ^{31}P NMR (1,4-dioxane): δ 66.8.

Dismutation of Compounds 22–27

A solution of 0.2 mmol of **16–21** in 1 mL of acetonitrile, methylene chloride, dioxane, benzene, or ether was added to 0.4 mmol of amide **4a–c**. Characteristic signals of cycloamidophosphites (**28–33**) appeared in the ^{31}P NMR spectrum of the reaction mixture (at 139.1–139.7 ppm

for methyl derivatives, at 140.0–140.8 ppm for ethyl derivatives, at 134.9–135.2 ppm for piperidyl derivatives, and at 135.8–136.6 ppm for morpholyl derivatives), as well as signals in the range typical for phosphorous acid triamides formed during the cyclization. The dismutation was considered completed when the signal of phosphorous acid ester diamide (at 128–132 ppm) disappeared and only the signals of phosphorous acid diester monoamides (135–140 ppm) and phosphorous acid triamides (115–122 ppm) remained in the spectrum.

Cyclo[bis-(1,6-naphthylenepiperidylamidophosphite)] (29b)

Yield 39%. Oily substance. R_f 0.72 (A). ^{1}H NMR: δ 1.53 m br (12H, CH_2), 3.34 t (8H, CH_2-N, $^3J_{PH}$ 8.3 Hz), 7.11 d (2H, C(2)H, $^3J_{H(2)-H(3)}$ 7.7 Hz), 7.28 d (2H, C(7)H, $^3J_{H(7)-H(8)}$ 9.9 Hz), 7.37 t (2H, C(3)H, $^3J_{H(2)-H(3)}$ 7.7 Hz, $^3J_{H(3)-H(4)}$ 8.8 Hz), 7.45 s (2H, C(5)H), 8.17 d (2H, C(4)H, $^3J_{H(3)-H(4)}$ 8.8 Hz), 8.21 d (2H, C(8)H, $^3J_{H(7)-H(8)}$ 9.9 Hz). ^{31}P NMR (C_6H_6): δ 135.7.

Cyclo[bis-(1,3-naphthylenepiperidylamidophosphite)] (30b)

Yield 41%. M.p.101–103°C. R_f 0.70 (A). ^{1}H NMR: δ 1.41 m br (12H, CH_2), 3.19 t (8H, CH_2-N, $^3J_{PH}$ 8.2, 7.7 Hz), 7.05 c (2H, C(2)H), 7.2 m br (4H, C(6,7)H), 7.37 d (2H, C(4)H), 7.62 d (2H, C(5)H), 8.1 d (2H, C(8)H). ^{13}C NMR: δ 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). ^{31}P NMR (C_6H_6: δ 135.5. Anal. calcd for $C_{30}H_{32}N_2O_4P_2 \cdot 0.25C_5H_{11}N$: C, 65.93; H, 5.90; N, 5.13. Found: C, 64.97; H, 6.21; N, 5.76.

Cyclo[Bis(2,6-naphthylenepiperidylamidophosphite)] (32b)

Yield 28%. M.p. 106–108°C. R_f 0.86 (B). ^{1}H NMR: δ 1.5 d br (12H, CH_2), 3.29 m br (8H, CH_2-N, $^3J_{PH}$ 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). ^{31}P NMR (C_6H_6): δ 136.6. Anal. calcd for $C_{30}H_{32}N_2O_4P_2$: C, 65.93; H, 5.90; N, 5.13. Found: C, 65.87; H, 5.92; N, 5.15.

Cyclo[Bis(2,6-naphthylenemorpholylamidophosphite)] (32d)

Yield 20%. Oily substance. ^{1}H NMR: δ 3.36 m br (8H, CH_2-N, $^3J_{PH}$ 5.5, 6.0 Hz), 3.65 d br (8H, CH_2-O), 7.24 d (4H, C(3,7)H), 4.45 s (4H, C(1,5)H), 7.68 d (4H, C(4,8)H). ^{31}P NMR (CH_2Cl_2): δ 135.2. and showed that the steric energies calculated for compounds **5–7** and **22–27** are

higher than for compounds **8–10** and **28–33**. The results of calculations are presented in Table III, Table IV.

The described process depends on many factors: aromatic skeleton, substituent at the phosphorus atom, solvent, and conjugation in the initial molecule (which is the determining factor). Derivatives of condensed aromatic systems dismutate more rapidly than their mononuclear analogues. Amide derivatives with aliphatic substituents at the nitrogen atom undergo dismutation more readily than their heterocyclic analogues. In methylene chloride, the process proceeds most rapidly regardless of the aromatic component and the substituent at the phosphorus atom. Apolar solvents (benzene, diethyl ether) do not favor dismutation. Temperature has no effect on the time of dismutation, and catalyst decreases it by a factor of 1.5–2.

REFERENCES

[1] E. E. Nifantyev, E. N. Rasadkina, P. V. Slitikov, and L. K. Vasyanina, *Phosphorus, Sulfur, and Silicon*, **178,** 2465 (2003).
[2] E. E. Nifantyev, E. N. Rasadkina, Yu. B. Evdokimenkova, V. K. Belsky, A. I. Stash, and L. K. Vasyanina, *Zh. Obshch. Khim.*, **71,** 203 (2001).
[3] E. E. Nifantyev, E. N. Rasadkina, and Yu. B. Evdokimenkova, *Zh. Obsch. Khim.*, **71,** 401 (2001).
[4] E. E. Nifantyev, E. N. Rasadkina, Y. B. Evdokimenkova, A. I. Stash, V. K. Belsky, and L. K. Vasyanina, *Heteroatom Chem.*, **14,** 404 (2003).
[5] E. E. Nifantyev, E. N. Rasadkina, Yu. B. Evdokimenkova, V. K. Belsky, A. I. Stash, and L. K. Vasyanina, *Zh. Obshch. Khim.*, **74,** 203 (2004).
[6] E. E. Nifantiev, M. K. Grachev, and S. Yu Burmistrov, *Chem. Rev.*, **100,** 3755 (2000).
[7] E. E. Nifantyev, E. N. Rasadkina, and I. V. Yankovich, *Zh. Obshch. Khim.*, **67,** 1812 (1997).
[8] E. E. Nifantyev, E. N. Rasadkina, I. V. Yankovich, L. K. Vasyanina, V. K. Belsky, and A. I. Stash, *Zh. Obshch. Khim.*, **69,** 36 (1999).
[9] E. E. Nifantyev, S. V. Suvorkin, E. N. Rasadkina, O. V. Selyutina, and A. V. Shishin, *Zh. Obshch. Khim.*, **72,** 1263 (2002).
[10] J. W. Steed and J. L. Atwood, *Supramolecular Chemistry* (John Wiley & Sons, Ltd., 2000) p. 26.
[11] S. Yu. Burmistrov and Yu. B. Evdokimenkova, *Candidate's Dissertation in Chemistry*. (Moscow, 1993).
[12] B. H. Hong, J. Y. Lee, S. J. Cho, Y. Yun, and K. S. Kim, *J. Org. Chem.* **64,** 5661 (1991).
[13] E. N. Rasadkina, P. V. Slitikov, M. S. Melnik, and E. E. Nifantyev, *Zh. Obshch. Khim.*, **74** (2004).
[14] E. N. Rasadkina, P. V. Slitikov, M. P. Pechkina, L. K. Vasyanina, and E. E. Nifantyev, *Zh. Obshch. Khim.* (in press).
[15] E. Fluck, J. R. van Waser, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81,** 6363 (1959).
[16] H. Noth and H. J. Vetter, *Chem. Ber.*, **98,** 1981 (1965).
[17] R. Burgada, *Ann. Chem.*, **8,** 363 (1963).
[18] S. Yu. Burmistrov and Yu. B. Evdokimenkova, *Candidate's Dissertation in Chemistry*. (Moscow, 2001).