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To the 80th Anniversary of B.I. Ionin

Synthesis of Organophosphorus Compounds Based on the Reaction of Elemental Phosphorus with Proton-Donor Reagents

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Abstract—Reaction of elemental (white) phosphorus with proton-donor reagents has been studied. The following organophosphorus compounds containing P–O and P–S bonds have been synthesized: metal hypophosphites and phosphites, and ammonium salts of *O,O'*-diesters of dithiophosphoric, *S,S'*-diphenyldithiophosphoric, *S,S'*-dialkyltetrathiophosphoric, *O,O'*-alkylidenedithiophosphoric acids, and octathiotetraphosphetane. The reaction products include highly efficient inhibitors of steel corrosion with carbonic acid and hydrogen sulfide as well as compounds showing fungicide, anticancer, and anti-inflammatory activity.

Keywords: white phosphorus, amines, proton-donor reagent, hypophosphite, phosphite, corrosion inhibitor

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Synthesis of organophosphorus compounds from elemental phosphorus (majorly from its most reactive form, white phosphorus) has drawn much attention due to its simplicity and the possibility to convert the element into a complex organophosphorus molecule in a single step. Moreover, such an approach is ecologically friendly and economically sound because it avoids formation of toxic and harmful side products: hydrogen chloride and hydrogen sulfide.

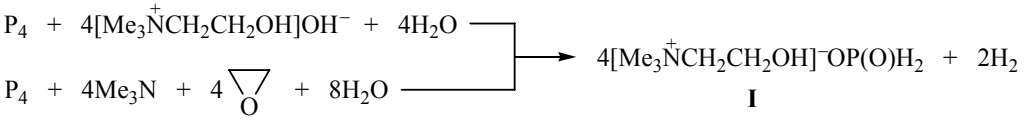
We have elaborated the approach to prepare organophosphorus compounds containing P–O and P–S bonds directly from elemental (white) phosphorus by selecting the appropriate proton-donor, nucleophilic, and electrophilic reagents. Realization of this approach opens a way to the synthesis of a variety of practically useful compounds, such as reducing agents for chemical nickel-plating of metals, antioxidants, vulcanization activators, foam stabilizers, photoreagents, light- and thermostabilizers, additives for lubricating oils, corrosion and salt deposition inhibitors, drugs, etc.

Using the proposed approach, we have synthesized different types of organophosphorus compounds: metal hypophosphites and phosphites as well as ammonium salts of *O,O'*-diesters of dithiophosphoric, *S,S'*-diphenyldithiophosphoric, *S,S'*-dialkyltetrathiophosphoric, *O,O'*-alkylidenedithiophosphoric acids, and octathiotetraphosphetane; some of the prepared compounds possess practically useful properties [1–8]. This work extends a series of studies of the reactions of white phosphorus with proton-donor reagents; herein we summarize the earlier obtained data and report on new results.

Reaction of white phosphorus with aqueous solution of β-hydroxyethyltriethylammonium hydroxide (choline). It is known that splitting of the P–P bonds of P_4 molecule tetrahedron by nucleophilic reagents (for example, hydroxide anion) yields phosphide anion. The latter, being a strong base, can further attack neutral P_4 molecule to stabilize the negative charge via formation of oligomeric phosphides in the absence of other electrophilic compounds. In the aqueous medium, an unstable intermediate is formed, which is slowly decomposed with evolution of hydrogen, phosphine, hypophosphite and phosphite ions [9].

Earlier we have worked out, optimized and industrially tested a general, ecologically friendly, and

Scheme 1.



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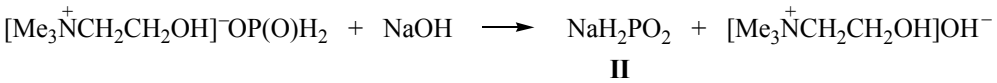

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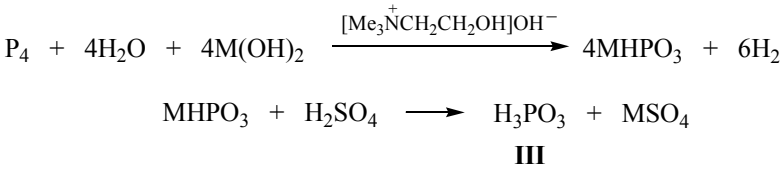


M = Ba, Ca.

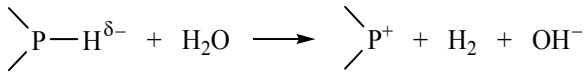
practically feasible one-pot synthesis of phosphorus(III) acids and their derivatives: phosphites and hypophosphites [1–5]. The method is based on the reaction of white phosphorus with β-hydroxylethyltriethylammonium hydroxide (choline) either introduced in the form of aqueous solution or formed *in situ* from the precursors: trimethylamine, ethylene oxide, and water. For example, the reaction under mild conditions (50–80°C, 9–10 h) has afforded choline hypophosphite **I** in up to 95% yield [1, 3] (Scheme 1).

The reaction of choline hypophosphite **I** with solution of NaOH in methanol has resulted in recovery of choline and formation of sodium hypophosphite **II** [2] (Scheme 2).

Under conditions of competitive formation of hypophosphite and phosphite structures, formation of the latter is known to be favorable in strongly alkaline media. The reaction of white phosphorus with choline and water in the presence of alkali earth metal hydroxides $Ba(OH)_2$ or $Ca(OH)_2$ has allowed obtaining phosphorous acid **III** in high yield [5] (Scheme 3).

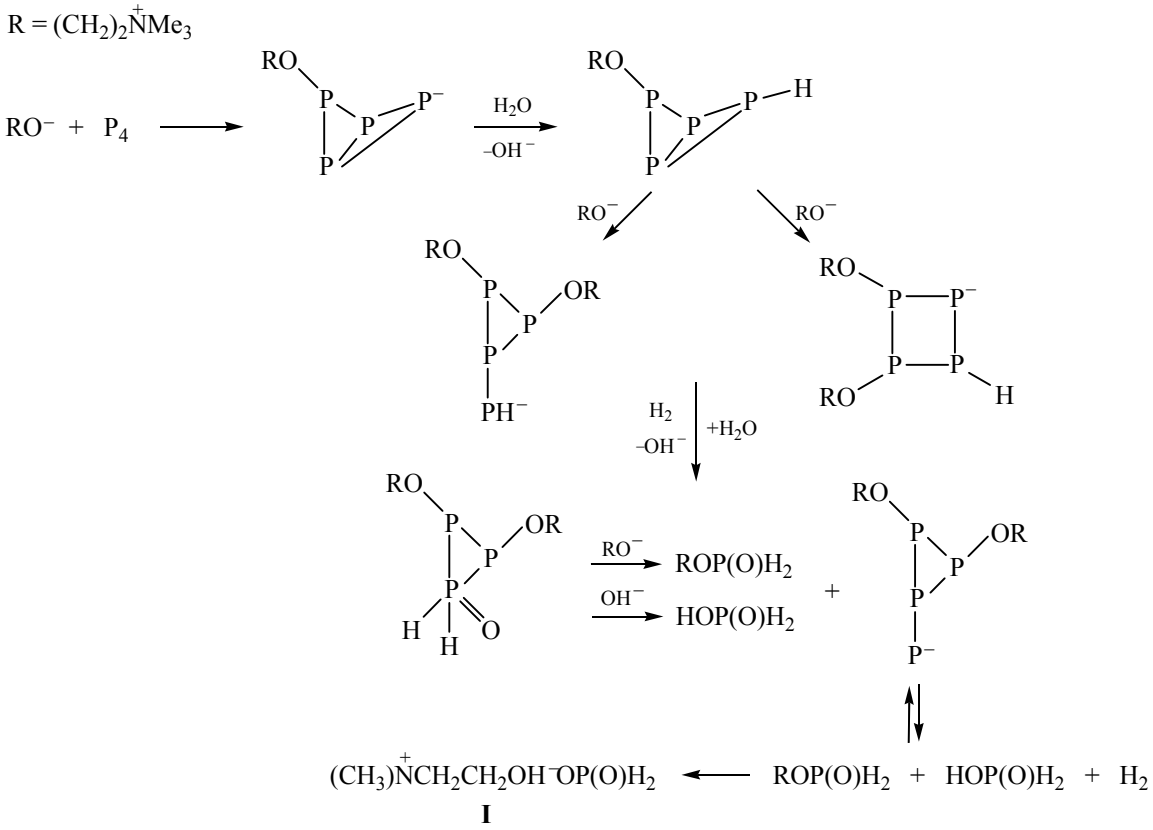
Preparation of hypophosphites and phosphites via the proposed method is not accompanied by formation of toxic phosphine; the process is wasteless (because of full conversion of phosphorus) and recyclable (the formed choline can be recovered). Hence, this method to prepare hypophosphites and phosphites in high yield in a single stage starting from elemental phosphorus is technologically and economically sound. Choline hypophosphite (I) was tested as a reducing agent in electrochemical nickel-plating industry [4].

Hydride shift in the reaction of white phosphorus with aqueous solution of choline. It is reasonable to assume that generation of hydrogen in the reaction of P_4 with aqueous solution of choline occurs via protonation of a P–H hydrogen atom of some intermediate by water molecule, provided that this hydrogen is partly negatively charged (hydride-like) allowing for the hydride shift.

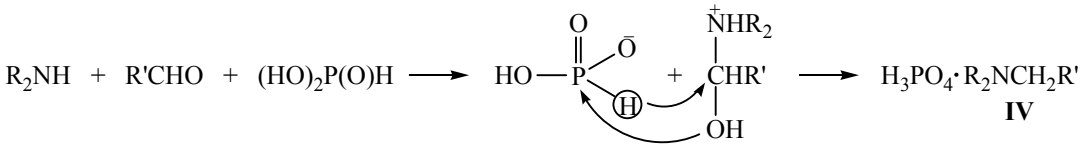


Mechanism of this process can involve the steps of phosphide anion generation followed by protonation with water and formation of four-phosphorus anions at the second stage of P–P bond cleavage. The competition between conventional protonation of the phosphide phosphorus atom and protonation of the hydride-like hydrogen atom to form hydrogen molecule can favor the latter reaction; this has been observed experimentally. The phosphide center is strongly sterically hindered by choline residues, blocking the interaction with the water molecule. Apparently, attraction of cationic sites of two choline residues to the phosphide group strongly contributes to the above-mentioned steric shielding and causes the special behavior of choline in the reaction with white phosphorus as compared to other nucleophiles (Scheme 4).

Scheme 4.



Scheme 5.



R = Et, –(CH2CH2OCH2CH2)–, R' = H, Ph.

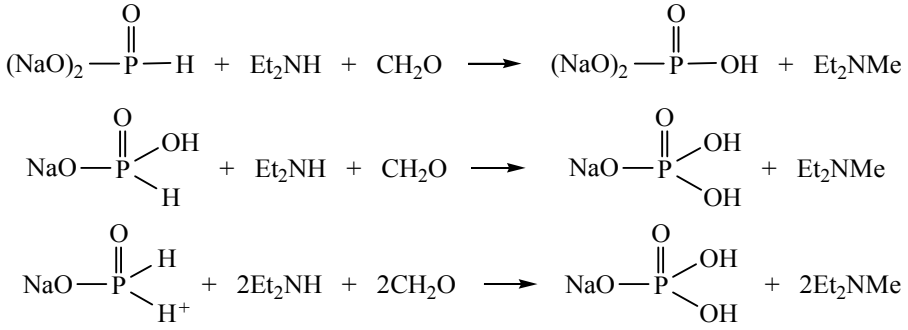
The choline salt of hypophosphorous acid **I** is formed both via hydrolysis of the choline ester of the acid and via neutralization of free acid $H_2P(O)OH$ with choline [10].

When trimethylammonium cation in choline is replaced by other ammonium radicals R_3N^+ (R = Et, Bu, or $PhCH_2Me_2$) the shielding of phosphide center is so strong that the interaction of water with the hydride-like hydrogen becomes impossible, and the reaction follows another ways leading, in particular, to evolution of phosphine [11].

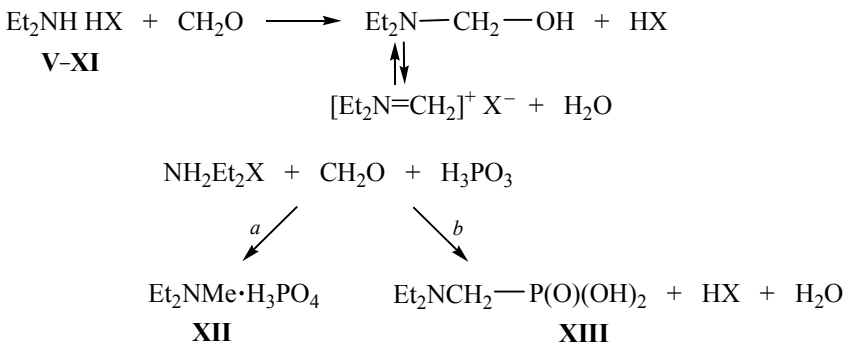
Hydride shift in the amine–aldehyde–phosphorous acid system. The ability of the P–H fragment to undergo hydride shift has been demonstrated in the case of secondary amine–aldehyde–phosphorous acid system. The only product of the reaction at 60–100°C is the corresponding tertiary ammonium phosphate **IV**. After treatment of the obtained salts with alkali, the corresponding tertiary amines have been isolated, whose structures have been confirmed by a combination of physico-chemical methods and elemental analysis (Scheme 5).

The reactions with di- and monosodium salts of phosphorous and hypophosphorous acids proceed similarly, yielding corresponding sodium salts of phosphoric acid and tertiary amines (Scheme 6).

Scheme 6.



Scheme 7.



HX = HCl (**V**), $0.5H_2SO_4$ (**VI**), H_2SO_4 (**VII**), $MeC_6H_4SO_2OH$ (**VIII**), CF_3COOH (**IX**), H_3PO_3 (**X**), MeCOOH (**XI**).

This reaction represents reductive alkylation of secondary amines with aldehydes [12] in the presence of the hydrogenating agent: phosphite or hypophosphite ion.

The reaction of phosphorous acid with aqueous solution of formaldehyde in the presence of various diethylammonium salts **V–XI** has been studied by ^{31}P NMR spectroscopy and the conditions favoring the hydride shift have been elucidated.

The oxymethyl derivative is formed in the reaction of salts **V–XI** with formaldehyde and free acid HX is simultaneously released, the latter determining pH of the reaction medium and concentration of the immonium cation. As basicity of the nitrogen atom in Et_2NHCH_2OH is strongly lowered due to conjugation of its lone-electron pair with the σ* orbital of the C–OH bond [13, 14], HX acid exists in the free form. In the diethylamine salt–formaldehyde–phosphorous acid system, two competitive processes can occur: phosphonaminoalkylation (Scheme 7, route *a*) and redox reaction (Scheme 7, route *b*), the predominant pathway being determined by pH of the medium (Scheme 7).

It has been shown that in the case of diethylammonium salts of weak acids **X** and **XI** the main process is oxidation of the phosphite anion into phosphate anion via hydride shift of hydrogen from phosphorus to the positively charged carbon atom of α-hydroxyalkylammonium cation to form salts of phosphoric acid **XII** (Scheme 7, route *a*), whereas for salts of stronger acids **V–IX** aminomethylation of the phosphorous acid leading to aminomethylphosphonous acid **XIII** predominates (Scheme 7, route *b*).

Reaction in the P_4–ROH–amine–sulfur system. Extending our studies on the methods to synthesize organophosphorus compounds starting from elemental phosphorus, we trialed the following combination of reagents: white phosphorus–proton donor–the conjugate base–the fourth reagent. Alcohols and phenols acted as proton donors. We anticipated that addition of an electrophilic reagent efficiently competing with protonation of the phosphide intermediate (result of the above-discussed P–P bond splitting in P_4) by the nucleophile or rapidly reacting with the P–H bond could enhance selectivity of the target product formation in the studied system.

Taking the white phosphorus–PhOH–PhONa–CCl_4 system as an example, we determined the range of phenols pK_a allowing their reaction with P_4 to obtain triarylphosphites [15]. Application of *N*-alkoxymethyldialkylamines and their heterocyclic analogs (piperidine and morpholine) in the white phosphorus–alcohol–sodium alkoxide system led to formation of a mixture of esters of aminomethylphosphonic and aminomethylphosphinic acids [16].

Using elemental sulfur was recognized as the best approach to prepare phosphorus-sulfur-containing compounds. In particular, convenient and highly selective synthesis of ammonium salts of *O,O'*-diesters of dithiophosphoric acids **XIV** was elaborated basing on cascade reactions in the white phosphorus–alcohol (phenol)–amine–elemental sulfur system [6, 17].

According to conventional mechanism of white phosphorus reactions with nucleophiles in proton-donor media, the opening of P_4 tetrahedron is followed by protonation of the phosphide center with alcohol to form a compound containing P–H bond and another nucleophile, RO^-. The presence of active sulfur capable of reacting with P–P, PH, or PH_2 fragments favored formation of more stable intermediates with P=S and P(S)SH fragments. Repetition of the described stages finally led to ammonium salts of *O,O'*-diesters of dithiophosphoric acids, valuable organophosphorus products.

$$P_4 + S_8 + 8ROH + 4R^1NR^2_2 \rightarrow 4(RO)_2PSH{\cdot}R^1NR^2_2 + 2H_2,$$

XIV

R = Et, *i*-Pr, *i*-Oct, $C_{12}H_{25}$, $C_{12–14}H_{25–29}$, Ph, *p*-MeC_6H_4, *p*-$C_9H_{19}C_6H_4$; $R^1 = R^2 = H$; $R^1 = R^2 = Et$; $R^1 = R^2 = Bu$; $R^1 = C_{12}H_{25}$, $R^2 = H$; $R^1 = Ph$, $R^2 = Me$; $R^1 = C_{25}H_{51}$, $R^2 = H$; $R^1 = C_{12–14}H_{25–29}$, $R^2 = Me$; $R^1 = H$, $R^2 = (–CH_2–)_5$; $R^1 = R^2 = (–CH–)_5$; $R^1 = CH_2NEt_2$, $R^2 = Et_2$; $R^1 = i$-$PrOCH_2$, $R^2 = Et_2$; $R^1 = CH_2N(–CH_2–)_5$, $R^2 = (–CH_2–)_5$; $R^1 = R^2 = CH_2CH_2OH$; $R^1 = H$, $R^2 = CH_2CH_2OH$; $R^1 = CH_2CH_2OH$, $R^2 = H$.

A wide range of aliphatic alcohols was introduced into the reaction in combination with ammonia, primary, secondary, tertiary aliphatic, aromatic, and heterocyclic amines as well as ethanolamines as the amine component. The reaction proceeded in the presence of amines with pK_a of 8.8 to 11.2. However, even when using less basic amines, like pyridine (pK_a 5.23) or *N,N'*-dimethylaniline (pK_a 5.06), the corresponding salts could be isolated. With aniline (pK_a 4.6), the corresponding salt of diethyldithiophosphoric acid was not obtained even after 30 h heating, the conversion of phosphorus being of 15%.

The elaborated one-pot method of ammonium salts of *O,O'*-diesters of dithiophosphoric acids **XIV** preparation is practically feasible and (unlike the industrial method of dialkyl- and diaryldithiophosphoric acids preparation via reaction of phosphorus pentasulfide with alcohols or phenols) does not result in evolution of hydrogen sulfide. The reaction can be carried out in toluene solution or in bulk. Ammonium salts of *O,O'*-diesters of dithiophosphoric acids **XIV** are obtained in 70–98% yield as crystalline compounds or viscous liquids. Their structure has been confirmed by ^1H, ^{31}P NMR (δ_P 108–115 ppm), and IR spectroscopy; the composition has been proved by elemental analysis.

When the reaction of white phosphorus and sulfur with *p*-cresol was performed in the presence of morpholine or pyridine in DMF, dimethylammonium salt of di(*p*-methylphenyl)dithiophosphoric acid **XV** was isolated, apparently formed via oxidative hydrolytic degradation of DMF in the presence of bases with elimination of dimethylamine.

$$P_4 + S_8 + n\text{-}MeC_6H_4OH \xrightarrow{DMF} (p\text{-}MeC_6H_4O)_2P(S)SH{\cdot}HNMe_2.$$

XV

The use of the $R_2NCH_2NR_2$ bisamines at the P_4–S_8–*i*-BuOH–$R_2NCH_2NR_2$ ratio of 1 : 2 : 2.2 : 0.5 allowed preparation of the corresponding bissalts **XVI**.

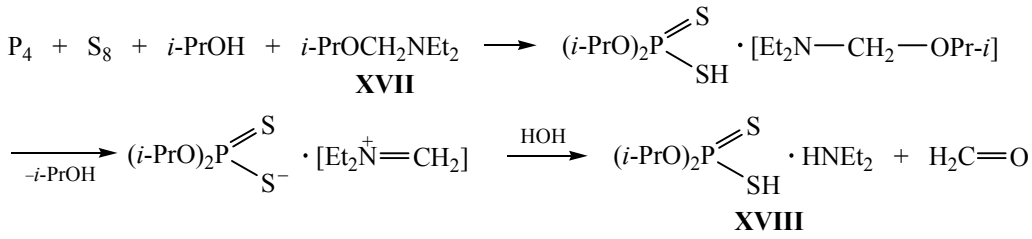
$$(i\text{-}BuO)_2\overset{S}{\overset{\|}{P}}–SH{\cdot}R_2NCH_2NR_2{\cdot}HS–\overset{S}{\overset{\|}{P}}(OBu\text{-}i)_2,$$

XVI

R = Et, $(–CH_2–)_5$.

N-Alkoxymethyldialkylamines were used as well for activation of sulfur; these amines are known for high reactivity and ability to eliminate an alkoxy anion [13]. Heating of white phosphorus with isopropanol, sulfur, and diethyl(isopropoxymethyl) amine **XVII** at 80–85°C resulted in diethylamine salt of diisopropyldithiophosphoric acid, due to hydrolysis of the initially formed immonium salt to yield the carbonyl compound and the secondary amine salt **XVIII** [17] (Scheme 8).

Scheme 8.



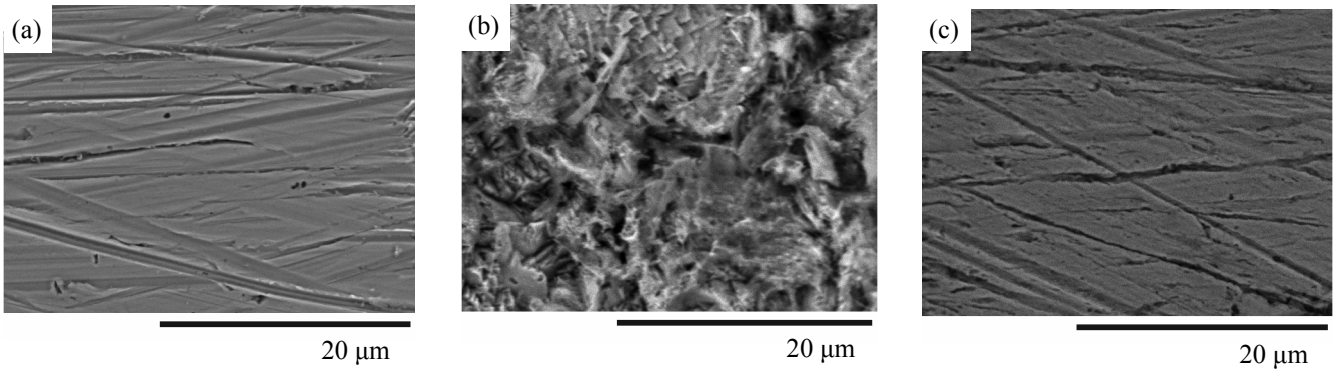
Salts of higher (C_{12}–C_{14}) dialkyldithiophosphoric acids **XIV** were obtained via reesterification of salts of lower (diisopropyl- or diisobutyldithiophosphoric) acids in the presence of acidic catalysts.

A series of the obtained ammonium salts of *O,O'*-dialkyldithiophosphoric acids **XIV** was examined as inhibitors of acidic corrosion of steel [19–21]. Among a variety of available inhibitors, these efficiently protecting steel in the media containing hydrogen sulfide or carbon dioxide are very limited; hence, elaboration of new efficient and universal inhibitors of steel corrosion is still a topical problem. We have found that ammonium salts of *O,O'*-dialkyldithiophosphoric acids obtained basing on the industrially available alcohols (*i*-$C_8H_{17}OH$, *i*-$C_{12-14}H_{25-29}OH$) and amines (Et_3N, $Et_2NC_{12-14}H_{25-29}$) are more efficient inhibitors of steel corrosion induced by carbonic acid and hydrogen sulfide as compared with the known Russian and foreign inhibitors. The figure displays representative samples of steel plates used in the test of triethylammonium salt of *O,O'*-diisooctyldithiophosphoric acid **XIV** as inhibitor of carbonic acid corrosion. The advantage of the obtained inhibitors is the enhanced protective efficiency with increasing medium temperature (30–80°C). Operation at elevated temperature is of special importance for oil extraction from deep strata [19].

Reaction in the P_4–RSH–amine–sulfur system. Replacement of alcohol with thiol in the white phosphorus–alcohol–amine–sulfur system affected the reaction course [22]. For instance, with isobutyl- or isopentylthiol **XIX**, two phosphorus-containing products **XIX** and **XX** were isolated. Four-membered monocyclic phosphorus derivatives, ammonium salts of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane **XXI** were obtained as minor products in 10–18% yield along with the major reaction product: ammonium salts of *S,S'*-dialkyltetrathiophosphoric acids (**XX**) (yield 78–80%) [8, 22–24]. The structure of the obtained salts was elucidated by a set of physico-chemical methods and (for selected products) additionally confirmed by X-ray diffraction analysis [22–24] (Scheme 9).

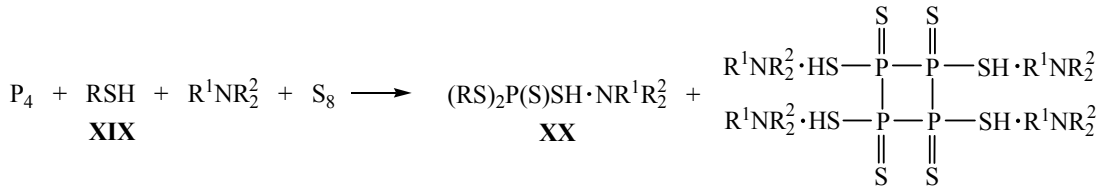
When aliphatic thiols were replaced by thiophenol, a hardly separable mixture of phosphorus-sulfur-containing products was obtained. In the absence of sulfur, the salts of *S,S'*-diesters of phosphoric acid were formed [7, 25].

Using triethylamine as an example, the possibility of ammonium salts of *S,S'*-diphenyldithiophosphoric acid **XXII** preparation via reaction of white phosphorus with thiophenol in the presence of air oxygen was demonstrated (Scheme 10).



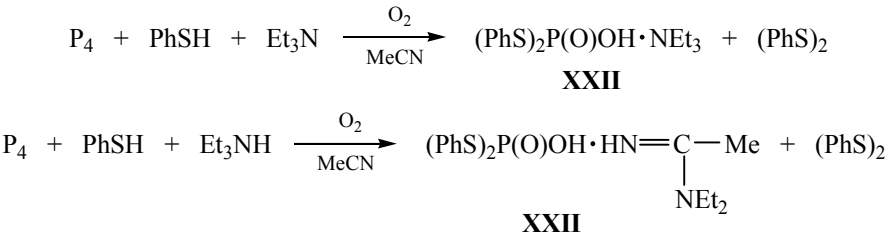
Soft steel plates: (a) pristine; (b) after 22 h incubation in corrosive medium; (c) after 22 h incubation in corrosive medium in the presence of 1 mg/L of salt **XIV**.

Scheme 9.

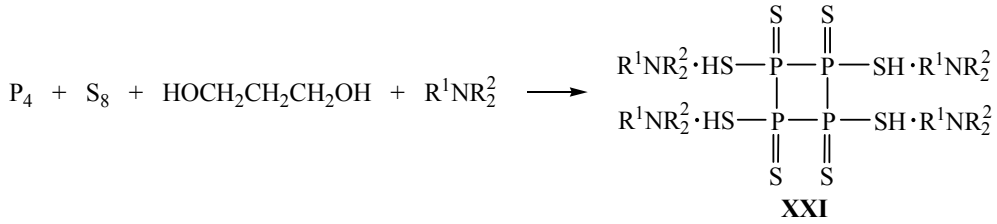


R = Bu, *i*-Am; $R^1 = R^2 = Et$; $R^1 = H$, $R^2 = (CH_2)_4$; $R^1 = Me$, $R^2 = (CH_2CH_2)_2O$; $R^1 = H$, $R^2 = Et$; $R^1 = H$, $R^2 = (CH_2)_5$.

Scheme 10.



Scheme 11.



$R^1 = R^2 = Et$; $R^1 = H$, $R^2 = –(CH_2)_5–$; $R^1 = H$, $R^2 = Et$; $R^1 = Me$, $R^2 = (CH_2CH_2)_2O$; $R^1 = CH_2C_6H_5$, $R^2 = Me$.

In the case of diethylamine, when the reaction was carried out in acetonitrile medium, the *N,N'*-diethylacetamidinium salt of *S,S'*-diphenyldithiophosphoric acid **XXIII** has been obtained. Formation of amidine likely occured via the reaction of acetonitrile with thiophenol in the presence of amines leading to thioimidate, followed by nucleophilic substitution of thiophenol residue in the latter by amines to yield *N,N'*-diethylacetamidine. (The formation of thioiminoesters via reaction of thiols with nitriles and their application in synthesis of amidines has been discussed earlier [26, 27]). The structure of salt **XXIII** was confirmed by X-ray diffraction analysis [7].

Reaction in the P_4–alkylene glycol–amine–sulfur system. Extending the study of white phosphorus reaction with proton-donor reagents, the reactions of P_4 with alkylene glycols were studied in the same system (Scheme 11).

The reaction in the P_4–1,3-propylene glycol–amine–S_8 system was performed in acetonitrile at 65–80°C during 8–10 h. The reaction proceeded with full conversion of white phosphorus and was not accompanied by evolution of hydrogen sulfide. After completion of the reaction and cooling the mixture, compounds with the ^{31}P NMR spectra signal at δ_P 120–122 ppm were isolated, corresponding to ammonium salts of octathiotetraphosphetane **XXI** [28]. Physicochemical and spectral parameters of salts **XXI** fully coincided with those for the compounds obtained via reaction of P_4, sulfur, and amines in the presence of thiols, which were earlier studied using IR/Raman, ^{31}P, and ^1H NMR spectroscopy as well as theoretically by DFT method [8, 23, 24].

To summarize, octathiotetraphosphetane derivatives were obtained via reaction of white phosphorus, sulfur, and amines both with aliphatic thiols and with alkylene glycols. The latter method was obviously more handy and preferable, since application of readily available and ecologically friendly 1,3-propylene glycol avoided use of toxic thiols.

Octathiotetraphosphetane salts **XXI** bearing different functional groups are of interest in view of many applications, including medicine and biology. These compounds form metal complexes with transition metal halogenides of groups I and VIII: Cu(I), Cu(II), Ag(I), Au(I), Fe(II), and Co(II). In cooperation with the research group from New-Mexico-Tech University (USA), the octathiotetraphosphetane salts were tested for bactericide, fungicide, anticancer, and anti-inflammatory activity. For ammonium salts of octathiotetraphosphetane and the metal derivatives, the fungicide (*Candida albicans*), anticancer (*HeLa*), and anti-inflammatory activity was revealed, depending on the nature of the metal or amine [27].

Our systematic study of the reactions of white phosphorus with proton-donor reagents allowed to work out and to optimize highly selective and ecologically friendly methods for preparation of valuable organophosphorus products directly from elemental phosphorus, avoiding evolution of hydrogen sulfide and/or phosphine.

EXPERIMENTAL

IR spectra were recorded with a Tensor 27 (Bruker) Fourier spectrometer in KBr at 4000–400 cm^{-1}. ^1H NMR spectra were registered using a Bruker MSL-500 (500.13 MHz) spectrometer with residual protons of the deuterated solvent as reference. ^{31}P NMR spectra were recorded with a Bruker MSL-400 (161.97 MHz) spectrometer, the internal references being TMS for (^1H) and 85% H_3PO_4 (^{31}P). C, H, N, and S elemental analysis was performed with a CHN-3 analyzer, content of phosphorus was determined via standard pyrolysis method.

Reaction of sodium hypophosphite with diethylamine and formaldehyde. 20.6 mL of diethylamine was added dropwise to 13.1 mL of 41% solution of formaldehyde at cooling (≤30°C). 10.6 g of NaH_2PO_2 was added to the obtained methylol derivative, and the reaction mixture was heated at 90–95°C during 10 h. The formed precipitate was filtered off and washed with acetone to give 11.9 g (82%) of NaH_2PO_4. ^{31}P NMR spectrum, δ_P, ppm: 4.1. Found, %: H 1.91; P 26.14. H_2NaO_4P. Calculated, %: H 1.67; P 25.83.

Reaction of disodium salt of phosphorous acid with diethylamine and formaldehyde. 27 mL of 41% formaldehyde solution was added dropwise to a mixture of 12.6 g disodium phosphite and 10.3 mL of diethylamine, and the mixture was self-heated to 50°C. The reaction mixture was cooled to room temperature and then heated to 90°C. The formed precipitate was filtered off and washed with acetone to give 9.6 g (80%) of Na_2HPO_4. ^{31}P NMR spectrum, δ_P, ppm: 4. Found, %: H 0.84; P 22.21. HNa_2O_4P. Calculated, %: H 0.70; P 21.83.

Reaction of monosodium salt of phosphorous acid with diethylamine and formaldehyde. Similarly, 10.2 g (85%) of NaH_2PO_4 was obtained from 10.4 g of NaH_2PO_3, 10.1 mL of diethylamine and 3.24 mL of 41% formaldehyde solution. ^{31}P NMR spectrum, δ_P, ppm: 4.1. Found, %: H 1.68; P 26.03. H_2NaO_4P. Calculated, %: H 1.67; P 25.84.

Reaction of phosphorous acid with morpholine and benzaldehyde. 8.7 g (0.1 mol) of morpholine was added at stirring to 8.2 g (0.1 mol) of phosphorous acid, the mixture was self-heated to 95°C. 10.18 mL (0.1 mol) of benzaldehyde was added dropwise to the obtained mixture, and the mixture was heated at 95–150°C during 1.5 h. 23.5 g (85%) of benzylmorpholine phosphate glassy mass was obtained. ^{31}P NMR spectrum, δ_P, ppm: 4.2. The obtained salt was dissolved in water, added dropwise to 24 g of NaOH under the layer of diethyl ether, and stirred at 35–40°C during 3.5 h. The formed Na_3PO_4 precipitate was filtered off and washed with diethyl ether (3 × 50 mL); ethereal extracts were combined with the filtrate, the solvent was removed, and the residue was distilled to obtain 12 g (79%) of benzylmorpholine, bp 124–125°C; n_D^{20} 1.5257. ^1H NMR spectrum (CCl_4), δ, ppm: 2.2–2.4 m (4H, CH_2OCH_2), 3.46–3.6 m (4H, CH_2NCH_2), 3.3 s (2H, CH_2N), 7.1 s (5H, C_6H_5). Found, %: C 74.12; H 8.06; N 8.32. $C_{11}H_{15}NO$. Calculated, %: C 74.57; H 8.47; N 7.91.

Reaction of phosphorous acid with morpholine and formaldehyde. 6.55 mL (0.1 mol) of 41% aqueous solution of formaldehyde was added dropwise to 8.7 g (0.1 mol) of morpholine. 8.2 g (0.1 mol) of phosphorous acid was then added, and the mixture was stirred during 0.5 h at 85–95°C. After removal of water 16.6 g (83%) of methylmorpholine phosphate viscous mass was isolated. ^{31}P NMR spectrum, δ_P, ppm: 4.2. Solution of 16.6 g of methylmorpholine phosphate in 10 mL of water was added dropwise to 12 g of NaOH in diethyl ether, and the mixture was incubated at 40°C during 3.5 h. The formed precipitate of Na_3PO_4 was filtered off and washed with ether (3 × 30 mL); ethereal extracts and filtrate were combined, ether was

removed, and the residue was distilled to give 6.7 g (80%) of methylmorpholine; bp 116–117°C, n_D^{20} 1.4325. Found, %: C 59.82; H 10.61, N 14.02. $C_5H_{11}NO$. Calculated, %: C 59.40; H 10.89, N 13.86.

Similarly, the reactions of phosphorous acid with diethylamine were performed in the presence of formaldehyde or benzaldehyde. 16.5 g (82.5%) of methyldiethylamine phosphate and 22.3 g (85.2%) of benzyldiethylamine phosphate, respectively, was isolated.

Reaction of phosphorous acid with diethylamine salts V–XI and formaldehyde. 6.38 mL of 41% aqueous solution of formaldehyde and 7.97 g of phosphorous acid were sequentially added to 50 mL of 1.94 mol/L solution of diethylamine salt **V–XI**. The reaction mixture was heated during 2 h at 80–100°C, water was removed; the viscous residue was sequentially washed with ether and acetone, and then incubated in vacuum. The products were analyzed using ^{31}P NMR spectroscopy.

Synthesis of diethylbisamine salt of diisobutyldithiophosphoric acid. Mixture of 1 g (32 mmol) of P_4, 2.2 g (69 mmol) of sulfur, 7.15 g (96 mmol) of isobutanol, and 2.5 g (16 mmol) of diethylbisamine was heated during 5 h at 70°C and during 6 h at 110–115°C. The excess of alcohol was removed in vacuum. The precipitated crystals of diethylbisamine salt of diisobutyldithiophosphoric acid were separated by filtration and washed with low-boiling petroleum ether. Yield 9.2 g (89%), mp 86–87°C. ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J,* Hz): 0.6 d [24H, $(CH_3)_2$, *J* 6 Hz], 0.9 t (12H, $\underline{CH_3}CH_2$, *J* 14 Hz), 1.36–1.9 m (4H, CH), 2.4 q (8H, $CH_3\underline{CH_2}$), 3.5–3.8 (10H, CH_2O and NCH_2N). ^{31}P NMR spectrum, δ_P, ppm: 113. Found, %: C 47.16; H 9.75; N 3.89; P 9.15; S 20.53. $C_{25}H_{60}N_2O_4P_2S_4$. Calculated, %: C 46.72; H 9.34; N 4.36; P 9.65; S 19.93.

Synthesis of dipiperidinebisamine salt of diisobutyldithiophosphoric acid. Similarly, 8.3 g (78%) of dipiperidinebisamine salt of diisobutyldithiophosphoric acid was obtained (mp 94–95°C) from 1 g (32 mmol) of P_4, 2.2 g (69 mmol) of sulfur, 7.15 g (96 mmol) of isobutanol, and 2.9 g (16 mmol) of piperidinebisamine. ^{1}H NMR spectrum (C_6D_6), δ, ppm (*J,* Hz): 0.66 d [24H, $(CH_3)_2$, *J* 6 Hz], 0.83–1.33 m (12H, $CH_2CH_2CH_2$), 1.4–1.9 m (4H, CH), 2.53–2.88 m (8H, CH_2NCH_2), 3.5–3.78 m (10H, NCH_2N and CH_2O). ^{31}P NMR spectrum, δ_P, ppm: 111. Found, %: C 48.33; H 9.46; N 4.15; P 8.96; S 19.69. $C_{27}H_{60}N_2O_4P_2S_4$. Calculated, %: C 48.65; H 9.01; N 4.20; P 9.31; S 19.22.

Synthesis of dimethylammonium salt of di(*p*-tolyl)dithiophosphoric acid. *a.* Mixture of 1.8 g (58 mmol) of P_4, 3.6 g (112.5 mmol) of sulfur, 12.6 g (117 mmol) of *p*-cresol, 5.6 g (64 mmol) of morpholine, and 2.4 g (33 mol) of DMF was heated during 4 h at 60°C, during 5 h at 80–90°C, and during 5 h at 100–120°C. Excess of CH_3CN was added to the reaction mixture. 8.2 g (70% with respect to DMF) of transparent crystals of dimethylammonium salt of di(*p*-tolyl)dithiophosphoric acid precipitated upon cooling, mp 146–147°C (CH_3CN). IR spectrum, ν, cm^{-1}: 680, 700 (P=S), 1600 (P–O–Ar), 2420, 2780 (S–H). ^{1}H NMR spectrum (CD_3CN), **δ,** ppm: 2.3 s (6H, $\underline{CH_3}C_6H_4O$), 2.6 s [6H, $(CH_3)_2N$], 7.13 s (8H, C_6H_4O). ^{31}P NMR spectrum, δ_P, ppm: 108. Found, %: C 54.48; H 6.20; N 3.88; P 9.24; S 17.65. $C_{16}H_{22}NO_2PS_2$. Calculated, %: C 54.08; H 6.19; N 3.94; P 8.73; S 18.03.

b. Mixture of 2 g (64.5 mmol) of P_4, 4 g (115 mmol) of sulfur, 14 g (130 mmol) of *p*-cresol, 3 g (38 mmol) of pyridine, and 2 g (27 mmol) of DMF was heated during 10 h at 70–80°C and during 14 h at 90–120°C. After addition of acetonitrile, 0.4 g of unreacted sulfur was precipitated. ^{31}P NMR spectrum, δ_P, ppm: 108.6 (40), 50.2 (19.5), –16.44 (40.5). Low-boiling petroleum ether was added to the filtrate. After 2 days incubation, the lower layer crystallized to give 5.1 g (53% with respect to DMF) of dimethylammonium salt of di(*p*-tolyl)dithiophosphoric acid, mp 147–148°C (CH_3CN). IR spectrum, ν, cm^{-1}: 680, 700 (P=S), 1600 (P–O–Ar), 2420, 2780 (S–H). ^{1}H NMR spectrum (CD_3CN), δ, ppm: 2.3 s (6H, $\underline{CH_3}C_6H_4O$), 2.6 s [6H, $(CH_3)_2N$], 7.13 s (8H, C_6H_4O). ^{31}P NMR spectrum, δ_P, ppm: 108. Found, %: C 53.62; H 6.20; N 4.17; P 9.03; S 17.65. $C_{16}H_{22}NO_2PS_2$. Calculated, %: C 54.08; H 6.19; N 3.94; P 8.73; S 18.03.

Synthesis of diethylammonium salt of diisopropyldithiophosphoric acid (XVIII). Mixture of 1 g (32 mmol) of P_4, 2 g (62 mmol) of sulfur, 5 g (35 mmol) of diethyl(isopropoxymethyl) amine, and 10 mL of isopropanol was heated during 0.5 h at 40–50°C and during 20 h at 80–85°C; the mixture was evaporated under water-jet pump vacuum, and petroleum ether was added. The reaction mixture was crystallized to give 7.2 g (78%) of diethylammonium salt of diisopropyldithiophosphoric acid **XVIII**, mp 92–93°C (ether). IR spectrum, ν, cm^{-1}: 640 (P=S). ^{1}H NMR

spectrum (CD_3CN), δ, ppm (*J,* Hz): 1.23 d (12H, CH_3, *J* 6.23 Hz), 1.33 t (6H, CH_3CH_2, *J* 7.1 Hz), 3.04–3.13 m (4H, CH_2N^+), 4.6–4.71 m (2H, CH). ^{31}P NMR spectrum, δ_P, ppm: 115. Found, %: C 41.96; H 9.53; N 4.83; P 10.3; S 22.5. $C_{10}H_{26}NO_2PS_2$. Calculated, %: C 41.81; H 9.06; N 4.88; P 10.8; S 22.29.

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