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ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of Nitrogen-containing Metal Dithiophosphates

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Abstract—Problems associated with synthesis of metal complexes and salts of dithiophosphates containing phosphorus, sulfur, and nitrogen heteroatoms and a sterically hindered hydroxy group in their molecule are considered.

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A particular place among chemical compounds serving as additives to oils, fuels, and polymeric materials is occupied by alkyl aryl dithiophosphates containing various functional groups and variable-valence metals in their molecules.

The reason is that these compounds are highly efficient and polyfunctional and can serve as antioxidant and aniticorrosive additives to oils and thermo- and photostabilizers, as well as quenchers for polymeric materials [1–4].

It is known that the efficiency and polyfunctionality of organic metal dithiophosphates depend not only on the nature of a metal contained in the complex, but also on functional groups in the chemical structure of the ligand environment of the central metal atom [5–7].

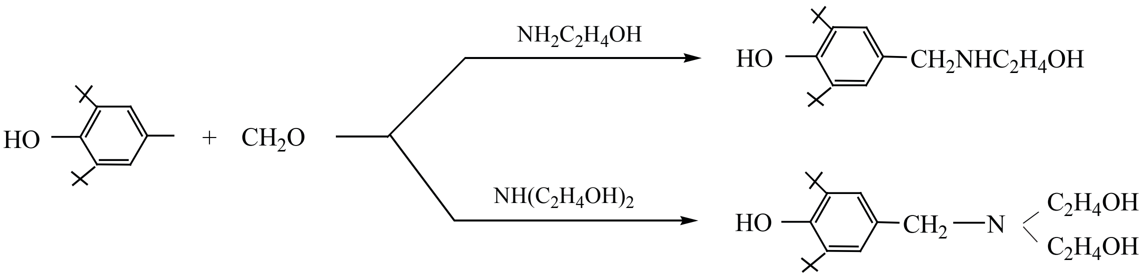
Stabilizing additives must contain various functional groups in their molecules, e.g., shielded hydroxy groups and P, S, and N heteroatoms acting by various mechanisms. Appropriate combination of these groups gives rise to synergism and enhances the polyfunctionality of the influence exerted by compounds of this kind.

For this purpose, we synthesized in this study organic compounds having in their molecules shielded hydroxy groups, heteroatoms (of phosphorus, sulfur, and nitrogen), and variable-valence metals.

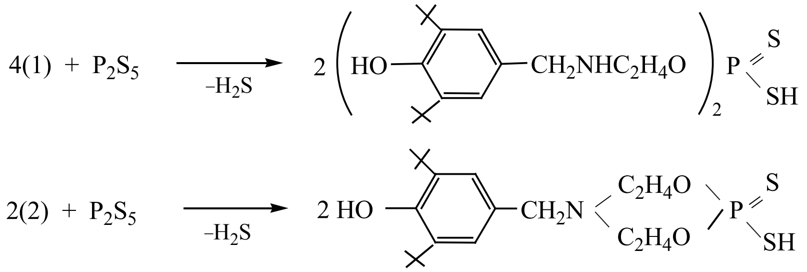
We first synthesized amino methyl derivatives (Mannich bases) by the reaction of 2,6-di-*tert*-butylphenol, formaldehyde, and mono- and diethylamines (Scheme 1).

The reaction was performed in benzene at 70–85°C in the course of 2.0–2.5 h [8]. The analytical and physicochemical characteristics of Mannich bases are listed in Table 1. The compounds obtained were used in the phosphosulfuration reaction with P_2S_5, which occurred by Scheme 2.

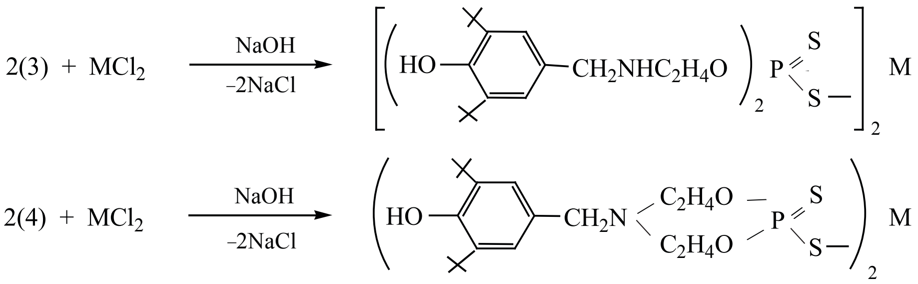
Scheme 1.



Scheme 2.



Scheme 3.



M = Ni, Co, Cu, Zn.

The O,O^1-dialkyldithiophosphoric acids were further neutralized with an aqueous solution of NaOH and converted by an exchange reaction to their metal salts or complexes (Scheme 3).

The course of these reactions and their intermediate and final products were studied by analytical and spectral (IR spectroscopy, ^{1}H NMR spectrometry) methods.

Our interpretation of the results of analyses of both intermediate and final products unambiguously evidences that the structure of the resulting Mannich bases and metal dithiophosphates and complexes on their basis is in agreement with the structures we suggest.

EXPERIMENTAL

IR spectra were measured with Specord M-80 and IRS-226 (CsI) spectrophotometers, and ^{1}H NMR spectra, with a Tesla BS-487 C spectrometer in CCl_4 (working frequency 80 MHz, HMDS as standard).

Phosphosulfuration of cycloalkylphenols. The phosphosulfuration of Mannich bases **1** and **2** with phosphorus pentasulfide was performed in a reactor equipped with a stirrer, reflux condenser, and lines for delivery of reagents and removal of hydrogen sulfide [9].

Table 1. Physicochemical and analytical characteristics of Mannich bases and O,O1-dialkyl dithiophosphoric acids

Compound	Yield, wt %	mp, °C	Empirical formula	Elemental composition, %			
				P		S	
				found	calculated	found	calculated
1	94–95	137–140	$C_{17}H_{28}O_2N$	–	–	–	–
2	95–96	100–103	$C_{18}H_{33}O_3N$	–	–	–	–
3	91–93	99–101	$C_{34}H_{57}O_4N_2PS_2$	5.11 5.24	4.75	10.01 10.13	9.81
4	89–90	140–142	$C_{19}H_{32}O_3NPS_2$	7.68 7.71	7.43	15.52 15.60	15.35

Table 2. Physicochemical and analytical characteristics of metal O,O^1-dithiophosphates

Compound	Yield, wt %	mp, °C	Empirical formula	Elemental composition, %					
				P		S		Ni	
				found	calculated	found	calculated	found	calculated
3-Ni	97.2	90–92	$C_{68}H_{112}O_8N_4P_2S_4Ni$	4.88 5.04	4.56	9.13 9.17	9.41	4.04 4.09	4.31
3-Co	92.7	130–132	$C_{68}H_{112}O_8N_4P_2S_4Co$	4.91 5.00	4.56	9.10 9.14	9.41	–	–
3-Cu	91.8	150–152	$C_{68}H_{112}O_8N_4P_2S_4Cu$	4.99 5.13	4.54	9.13 9.15	9.37	–	–
4-Ni	90.2	53–55	$C_{38}H_{60}O_6N_2P_2S_4Ni$	6.68 6.71	6.98	14.11 14.17	14.40	6.40	6.61
4-Co	87.8	98–100	$C_{38}H_{60}O_6N_2P_2S_4Co$	6.69 6.71	6.98	14.13 14.17	14.40	–	–
4-Cu	93.4	74–75	$C_{38}H_{60}O_6N_2P_2S_4Cu$	7.21 7.30	6.94	14.61 16.68	14.33	–	–
4-Zn	94.2	138–140	$C_{38}H_{60}O_6N_2P_2S_4Zn$	6.68 6.71	6.92	14.53 14.60	14.29	–	–

Table 3. Results of tests of the metal dithiophosphates synthesized as additive to M-8 motor oil (T = 200°C, τ = 10 h)

Formulation	Amount of additive, wt %	Viscosity at 10°C, mm^2 s^{-1}		Increase in viscosity, %	Amount of sediment, %
		initial	upon oxidation		
M-8	–	7.95	9.23	16.10	4.47
M-8+(3)-Zn	0.10	7.96	10.50	32.08	4.27
	0.25	7.95	10.08	26.79	3.76
	0.50	7.96	8.98	12.81	2.90
M-8+(3)-Ni	0.20	7.95	9.27	16.60	3.42
	0.40	7.96	9.08	14.08	3.08
	0.50	8.01	8.99	12.23	2.76
M-8+(4)-Co	0.10	7.96	10.50	16.10	4.20
	0.20	7.99	10.21	16.00	4.23
	0.50	7.01	10.08	16.00	4.31
	1.00	8.03	9.76	15.97	4.30
M-8+(4)-Ni	0.10	7.95	9.21	15.85	3.45
	0.20	7.96	9.17	15.20	3.38
	0.50	8.04	9.12	13.43	2.90
	1.00	8.27	9.34	12.94	2.76
M-8 + IKhP -21	2.1	8.01	9.34	16.23	2.49

A calculated amount of Mannich bases (4 mol for compound **1** and 2 mol for **2**) was charged into the reactor, to which the solvent (toluene) was also delivered. The mixture was heated to 70–80°C and finely ground P_2S_5 (or its suspension in toluene) was added in portions under agitation. After the addition of P_2S_5 was complete, the mixture was heated to the boiling point of the solvent and the reaction continued until H_2S evolution ceased. The reaction was performed under a somewhat reduced pressure (650–670 mm Hg); after the reaction was complete, nitrogen was passed through the reaction mass during 20–30 min. H_2S released in the reaction was passed through an aqueous solution of $CdCl_2$ and the amount of the CdS precipitate was used to determine the amount of released H_2S, with the reaction course thus monitored. The analytical and physicochemical characteristics of O,O^1-dialkyl dithiophosphoric acids are listed in Table 1.

The IR spectra of compounds **1** and **2** show at 3680–3620 cm–1 a strong broad absorption band characteristic of vibrations of OH groups; stretching vibrations of the NH group appear at 3400–3380 cm^{-1}, and its deformation vibrations, at 1650–1600 cm^{-1}. At 1225–1250 cm^{-1}, there are absorption bands corresponding to skeletal vibrations of the *tert*-butyl group. The spectra contain absorption bands characteristic of pendular vibrations of the $–CH_2–$ group bonded in an aliphatic chain to a nitrogen atom ($–CH_2–N^*$) at 735–730 cm^{-1}, and deformation vibrations of this group bonded to a benzene ring at 1470–1460 cm^{-1}.

^1H NMR spectra of compounds **1** and **2** (CCl_4, δ, ppm): 6.95–6.98 (1H for shielded OH), 5.15 (1H for alcoholic OH of compound **1**) and 5.17 (2H for alcoholic OH of compound **2**), 3.2–3.4 (1H for NH group of compound **1**), 7.12–7.15 (3H for aromatic nucleus), and 1.70–1.72 (9H for *tert*-butyl group).

The IR spectra of compounds **3** and **4** contain, in addition to the bands observed for compounds **1** and **2**, a band of stretching vibrations of the S–H group at 2550–2500 cm^{-1}. In addition, there appear vibrations characteristic of the following groups (cm^{-1}): P–S (560–530), P=S (679–650), and P–O–C aryl (1190–1160).

^1H NMR spectra of compounds **3** and **4** (CCl_4, δ, ppm): 6.71–6.76 (2H for shielded OH), 3.05 (1H SH for compound **3**] and 3.10 [1H for compound (4)], 7.30–7.35 (6H for aromatic nucleus), 1.60–1.63 (18H for *tert*-butyl group), and 3.18–3.21 [2H for NH group of compound (3)].

Metal dithiophosphates. Taking into account that O,O^1-dialkyl dithiophosphoric acids are obtained in nearly theoretical yield, we subjected the acid to neutralization with a 10% NaOH solution directly in the toluene solution. Because the neutralization reaction is strongly exothermic, it is necessary to intensively cool the reaction mass. The alkali was delivered at such a rate that the reaction mass temperature did not rise to above 20–25°C; at higher temperatures, the acid is hydrolyzed. The neutralization was performed to pH 6–7 or weakly acid reaction, with the acidity of the medium determined at regular intervals of time.

After the reaction was complete and the reaction mixture was allowed to settle for 1.5–2.0 h, the organic layer was separated and the aqueous layer containing the sodium salt of an acid was delivered to the exchange reaction.

The neutralization equivalent was also used to determine the purity of O,O^1-dialkyl dithiophosphoric acids. It was found that the acids are characterized by a rather high purity (99.0–99.5%).

Metal salts and complexes of O,O^1-dialkylsubstituted dithiophosphoric acids were produced by the exchange reaction of a sodium salt of a disubstituted dithiophosphoric acid obtained in the preceding stage with a 70–75% aqueous solution of the corresponding metal chloride (at a 2 : 1 ratio). The reaction was performed at room temperature under agitation. As the metal chloride was supplied, salts and complexes of disubstituted dithiophosphates precipitated from solution. The precipitate was filtered off, washed with water, and dried at 60–70°C in a vacuum.

When cobalt complexes are to be obtained, it is preferable to perform the process in an alcoholic–aqueous medium at a (10–15) : 1 alcohol : water volume ratio.

Analytical and physicochemical characteristics of metal dithiophosphates are listed in Table 2.

An analysis of the IR spectra demonstrated that there are no bands associated with vibrations characteristic of the S–H group. Instead, the long-wavelength part of the spectra contains absorption bands typical of vibrations of the S–metal group. Stretching vibrations of S–Ni, S–Co, and S–Cu appear as a rather strong absorption band at 355–350, 325–320, and 330–325 cm^{-1}, respectively.

Metal dithiophosphates as antioxidants for motor oil. The compounds **3**–Ni, **3**–Co, **4**–Ni, and **4**–Zn were tested as antioxidant additives to M-8 motor oil in conformity with GOST (State Standard) 11063–77. As reference in tests under the same conditions served industrial additive IKhP-21, an analog of the compounds we synthesized. The test results are listed in Table 3.

Our tests demonstrated that all the dithiophosphates effectively inhibit the oxidation of M-8 oil and, event at four times lower concentrations, exhibit an inhibiting effect comparable with that of the widely industrially used IKhP-21 additive.

CONCLUSIONS

(1) Nitrogen-containing metal O,O^1-di-alkyl dithiophosphates were synthesized by phosphosulfuration of Mannich bases produced in the reaction of 2,6-di-*tert*-butylphenol and formaldehyde with mono- and diethanolamines.

(2) From dithiophosphorylated methylaminophenols were synthesized and characterized Ni, Co, Cu, and Zn metal complexes, which are potentially effective additives to motor oils and polyolefins.

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