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Abstract

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CHEMISTRY

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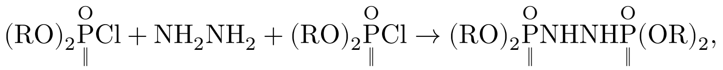
PHOSPHORUS-CONTAINING HYDRAZO AND AZO COMPOUNDS

We have previously described diazophosphonic esters and shown that the –N=N –bond contained in them has an electrophilic character, which is manifested in the ability of these compounds to readily add, in the presence of basic catalysts, such typical nucleophilic reagents as partial esters of phosphorous, malonic, acetoacetic, and cyanoacetic acids (^{1}).

In the present work we carried out the synthesis of esters of azodiphosphonic acids and investigated their ability to undergo addition reactions. Compounds of this type have been little studied. There are data on the preparation of the tetraphenyl ester of azodiphosphonic acid in connection with a study of the relationship between the color and structure of azo compounds (^{2}). Meanwhile, the carbon analogs–esters of azodicarboxylic acid–have long been known, and their reactivity in addition and diene-synthesis reactions has been studied in considerable detail ($^{3-6}$).

For the synthesis of esters of azodiphosphonic acids containing aliphatic radicals in the ester groups, we used the method of oxidation of esters of hydrazodiphosphonic acids.

Tetraalkyl esters of hydrazodiphosphonic acid were obtained by the interaction of acid chlorides of dialkylphosphonic acid with hydrazine



$$(\mathrm{RO})_2\overset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}\mathrm{Cl} + \mathrm{NH_2NH_2} + (\mathrm{RO})_2\overset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}\mathrm{Cl} \rightarrow (\mathrm{RO})_2\overset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}\mathrm{NHNH}\overset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}(\mathrm{OR})_2,$$

where $R = C_2H_5, n\text{-}C_4H_9, n\text{-}C_6H_{13}, n\text{-}C_8H_{17}$. Reactions of diethyl and dibutyl chlorophosphates with hydrazine were carried out in ethereal solution at 25–30°, and with dihexyl and dioctyl chlorophosphates at 40–45°. Symmetric hydrazodiphosphonic esters were isolated from the reaction mixture and purified by fractional precipitation from benzene solutions with hexane or petroleum ether.

The precipitation was repeated many times. The yield of tetraalkyl esters of hydrazodiphosphonic acid was 60-80% (Table 1).

In their IR spectra there are intense absorption bands characteristic of the groups: $P = O$ (1236–1220 cm^{-1}), P—O—Alk (1020 cm^{-1}), NH (3175–3195 cm^{-1}). The shift of the absorption band of the $P = O$ group into the long-wavelength region can be explained by the formation of an intramolecular hydrogen bond (^{7}).

For the oxidation of tetraalkyl esters of hydrazodiphosphonic acid, we used a saturated solution of potassium permanganate and bromine. In the first case the reactions were carried out at $0, -10, -15°$. Under these conditions it was not possible to obtain the target oxidation products.

Oxidation with bromine of tetraalkyl esters of hydrazodiphosphonic acid proceeds smoothly, and esters of azodiphosphonic acid were obtained in 30-60% yields.

Upon slow addition of bromine to an ethereal solution of the hydrazodiphosphonic ester ($t = -20; -15°$), bleaching of the bromine was at first observed, and then the solution gradually acquired a dark violet color. The reaction mixture was stirred to complete the oxidation for a period of

hours and was treated with dilute solutions of thiosulfate and soda, cooled to 0°, and with water. During the treatment the color of the ethereal solution was retained. After the ether had been distilled off, dark-violet oils remained. On chromatography of benzene solutions of the resulting oils on a column packed with aluminum oxide, a distinct

Table 1

Tetraalkyl esters of hydrazodiphosphoric and azodiphosphoric acids and hexaalkyl esters of hydrazotriphosphoric acid

Compound	Appearance	Yield, %	n_D^{20}	P, % found	P, % calculated	N, % found	N, % calculated
$(C_2H_5O)_2P(=O)NHNHP(=O)(OC_2H_5)_2$*	Viscous yellow oil	72.7	—	20.29; 20.20	20.30	8.99; 9.36	9.20
$(C_4H_9O)_2P(=O)NHNHP(=O)(OC_4H_9)_2$	Viscous yellow oil	59.6	—	14.47; 14.28	14.90	7.28; 7.40	6.73
$(C_6H_{13}O)_2P(=O)NHNHP(=O)(OC_6H_{13})_2$	Same	69.2	1.4580	11.41; 12.03	11.74	5.11	5.30
$(C_8H_{17}O)_2P(=O)NHNHP(=O)(OC_8H_{17})_2$**	Same	80.0	1.4600	9.40; 9.38	9.68	–	–

Compound	Appearance	Yield, %	n_D^{20}	P, % found	P, % calculated	N, % found	N, % calculated
$(C_2H_5O)_2P(=O)N=NP(=O)(OC_2H_5)_2$	Viscous violet-colored oil	30.7	1.4370	20.52; 20.38	20.57	–	–
$(C_4H_9O)_2P(=O)N=NP(=O)(OC_4H_9)_2$	Same	42.3	1.4470	14.28; 14.48	14.97	6.72; 6.75	6.76
$(C_6H_{13}O)_2P(=O)N=NP(=O)(OC_6H_{13})_2$	Viscous violet-colored oil	58.8	1.4489	11.55; 11.31	11.78	4.24; 4.55	5.30
$(C_8H_{17}O)_2P(=O)N=NP(=O)(OC_8H_{17})_2$	Same	61.2	1.4570	–	–	4.30; 4.40	4.38
$(C_2H_5O)_2P(=O)NHN[P(=O)(OC_2H_5)_2]_2$	Yellow oil	92.1	1.4460	20.88; 21.10		6.21; 6.27	6.30
$(C_4H_9O)_2P(=O)NHN[P(=O)(OC_2H_5)_2]_2$	Same	86.1	1.4390	18.73; 18.60	18.72	5.25; 5.08	5.6
$(C_8H_{17}O)_2P(=O)NHN[P(=O)(OC_2H_5)_2]_2$	Same	88.6	1.4450	15.50; 15.51	15.29	5.05; 5.15	4.6
$(C_4H_9O)_2P(=O)NHN[P(=O)(OC_4H_9)_2]_2$	Same	81.4		15.54; 15.52	15.29	–	–

* Found, %: C 31.67, H 7.21. Calculated, %: C 31.50, H 7.23. M.p. 55-56°.
** Found, %: C 60.03, H 10.90. Calculated, %: C 30.00, H 10.90.

zone colored violet appeared. The characteristics of the tetraalkyl esters of azodiphosphoric acid are given in Table 1. When the absorption curves of alcoholic solutions of the tetraalkyl esters of azodiphosphoric acid were recorded in the visible part of the spectrum, it was found that the absorption maxima of the tetraethyl and tetrabutyl esters of azodiphosphoric acid are located at 550 mμ. In the IR spectra of these compounds there are absorption bands characteristic of P=O (1280 cm^{-1}) and P—O—Alk (1200 cm^{-1}); the absorption band characteristic of the NH group is absent. The tetraalkyl esters of azodiphosphoric acid are unstable compounds. Their stability decreases as the amount of impurities in them increases. On distillation of the tetraethyl ester of azodiphosphoric acid, its decomposition occurred. During prolonged storage of the azodiphosphoric esters at room temperature, their gradual decomposition was also observed, accompanied by the evolution of nitrogen bubbles and a change in the color of the substance.

The addition of dialkyl phosphorous acids to the synthesized tetraalkyl esters of azodiphosphoric acid was carried out. Sodium dialkyl phosphite was used as the catalyst. To an ether solution of the starting substances, taken in an equimolecular ratio, an ether solution of sodium dialkyl phosphite was added dropwise. Heating of the reaction mixture and its gradual discoloration were observed. Purification of the obtained addition products, which were yellow oils, was carried out by heating with adsorbents—aluminum oxide and wood charcoal; their yield was 80-90% (see Table 1). The esters of hydrazotriphosphoric acid are soluble in most organic solvents and in water.

In the IR spectrum of the hexaethyl ester of hydrazotriphosphoric acid there are absorption bands characteristic of $P = O$, $P - O - Alk$, and NH groups.

From the investigation presented it is evident that the tetraalkyl esters of azodiphosphoric acid belong to compounds of electrophilic character, capable of the facile and quantitative addition of nucleophilic reagents.

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Note: Figure translations are in progress. See original paper for figures.

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