SYNTHESIS OF N-TETRAALKYLDIAMIDOPHOSPHONYL (AND-THIOPHOSPHONYL)IMIDOPHOSPHATES – SUBSTANCES WITH POTENTIAL HERBICIDAL AND DEFOLIANT ACTIVITY

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Experience has shown that some imidophosphates have herbicidal and defoliant activity [1-3]. In conducting a systematic study of the relationship of this activity to structure, we synthesized a series of N-dialkoxyphosphonylimidophosphates [4] and N-dialkoxythiophosphonylimidophosphates [5].

In the present work we described a series of imidophosphates of the following types: $(RO)_3P = NP(X)(NR_2')_2$, $(R_2N)_2P(OR) = NP(X)(NR_2'')_2$, $(R_2'N)P(OR_2) = NP(X)(NR_2'')_2$, $(R_2N)_3P=NP(X)(NR_2')_2$ (where X = O or S). Obviously, these compounds contain from two to five dialkylamino groups or zero, one, two, or three alkoxy groups. Imidophosphates are obtained from the corresponding trivalent phosphorus compounds and tetraalkyldiamidoazidophosphates (and –thiophosphates); for example,

$$(RO)_3P + (R_2'N)_2P(S)N_3 \rightarrow (RO)_3P{=}NP(S)(NR_2')_2$$

Compounds of the first type (where X=O) have been described earlier [6]. The phosphites were added to the reaction mixture in excess, in order to ensure completion of the reaction. Reactions were carried out in benzene at 50-60°C. In the reaction with tetraalkyldiamidoazidophosphates, a decrease in reactivity in comparison to the dialkylazidophosphates was observed. In the case of the tetraalkyldiamidoazidothiophosphates, the decrease in reactivity was still greater. Constants and yields are presented in Table 1.

During distillation of the imidophosphates containing alkoxy groups, imide–imide rearrangement is possible [6]:

$$(RO)PY_2{=}NP(X)(NR_2')_2 \rightarrow Y_2P(O)N{=}P(XR)(NR_2')_2$$
$$X = O \text{ or } S,\ Y = OR \text{ or } NR_2$$

However, IR spectra of the reaction mixtures prior to distillation were identical to the IR spectra of the distillates. The identities of all products were confirmed by TLC. In the IR spectra of imidophosphates I–V, there is an absorption band in the region of 1260-1290 cm^{-1} (P=N); for N-thiophosphonylimidophosphates VII–XIV the band appears in the region of 1250-1300 cm^{-1}, in agreement with data for N-phosphonyimidophosphates [7] and N-thiophosphonylimidophosphates [5]. The structures of imidophosphates I–V were confirmed by ^{31}P-NMR spectra. Correlation of the chemical shifts was accomplished by reference to available data [6, 8]. The results of analyses by the methods of IR and ^{31}P-NMR spectroscopy are included in Table 1.

In the synthesis of the tetraalkyldiamidoazidophosphates (and –thiophosphates), we introduced some changes in the described methods, allowing us to obtain these azides under milder conditions or to obtain them free of unreacted acid chlorides. The synthesis of tetraethyldiamidoazidophosphate [9], as well as that of tetramethyldiamidoazidophosphate [10], was carried out in pyridine; the indicated method was simplified by treating the initial acid chloride mixture with NaN_3 at ~20°, rather than boiling for several hours. Tetramethyldiamidoazidothiophosphate, described in [10], and tetraethyldiamidoazidothiophosphate were obtained by the method of [5], based on displacement of chlorine in the tetraalkyldiamidophosphoric acid chlorides by the azido group in DMF. It must be noted that tetraethyldiamidoazidothiophosphate, as obtained in [9] by boiling an acetone solution of the initial acid chloride with NaN_3, is impure and contains 2% chlorine. Constants and yields of the synthesized phosphoric acid azides are given in Table 2.

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TABLE 1

Compound No.	Formula	Yield, %	bp, °C (mm Hg)	n_D^{20}	d_4^{20}	MR		IR spectrum ν, cm^{-1}		^{31}P-NMR spectra δ, ppm; J, Hz		
						found	calc.	P=O	P=N	P_A	P_B	$J_{P_ANP_B}$
(I)	$(Et_2N)_3P_A=NP_B(O)(NEt_2)_2$	93	110 (2·10^{-3})	1,4580	1,0073	128,83	128,97	1200	1260	—19,0	—7,2	46,4
(II)	$(Et_2N)_2P_A(OEt)=NP_B(O)(NEt_2)_2$	75	112 (2·10^{-3})	1,4720	1,0072	118,30	118,45	1215	1275	—14,3	—8,3	44,0
(III)	$(Et_2N)P_A(OEt)_2=NP_B(O)(NEt_2)_2$	97	96 (1·10^{-3})	1,4620	1,0192	106,48	106,64	1200	1290	—6,4	—8,2	45,2
(IV)	$(Et_2N)_2P_A(OBu)=NP_B(O)(NEt_2)_2$	80	145 (1·10^{-2})	1,4710	1,0050	127,15	127,09	1215	1275	—13,9	—8,8	43,9
(V)	$(Et_2N)P_A(OBu)_2=NP_B(O)(NEt_2)_2$	91	120 (2·10^{3})	1,4615	1,2593	125,33	125,11	1200	1275	—6,4	—8,4	46,4
(VI)	$Ph_3P=NP(O)(NEt_2)_2$	96	95 †	—	—	—	—	1190 ‡	1260	—	—	—
(VII)	$(EtO)_3P=NP(S)(NMe_2)_2$	96	93 (1·10^{-3})	1,4857	1,1114	84,93	84,64	—	1300	—	—	—
(VIII)	$(Et_2N)P(OEt)_2=NP(S)(NMe_2)_2$	95	95 (1·10^{-3})	1,4910	1,0799	94,83	95,16	—	1280	—	—	—
(IX)	$(BuO)_3P=NP(S)(NMe_2)_2$	98	101 (1·10^{-3})	1,4765	1,0363	112,19	112,35	—	1280	—	—	—
(X)	$(Et_2N)_2P(OBu)=NP(S)(NMe_2)_2$	97	102 (1·10^{-3})	1,4960	1,0316	117,10	117,21	—	1255	—	—	—
(XI)	$(EtO)_3P=NP(S)(NEt_2)_2$	95	92 (1·10^{-3})	1,4843	1,0660	102,94	103,12	—	1280	—	—	—
(XII)	$(BuO)_3P=NP(S)(NEt_2)_2$	92	120 (1·10^{-3})	1,4785	1,0154	134,55	134,82	—	1280	—	—	—
(XIII)	$(Et_2N)_2P(OEt)=NP(S)(NEt_2)_2$	98	106 (1·10^{-3})	1,4980	1,0460	125,65	125,44	—	1255	—	—	—
(XIV)	$(Et_2N)_2P(OBu)=NP(S)(NEt_2)_2$	96	127 (1·10^{-3})	1,4950	1,0027	134,29	134,58	—	1250	—	—	—

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* For compounds I-III, V, and VI, satisfactory elemental analyses were obtained for C, H, and P; for compounds IV and VII-XIV, analyses were obtained only for P.

†Melting point is shown.

‡ IR spectrum in chloroform solution (0.2 mole/liter).

TABLE 2

Compound	Formula	Yield, %	bp, °C (p $1\cdot10^{-2}$ mm)	n_D^{20}	d_4^{20}	MR†	
						found	calculated
(XV)	$(Et_2N)_2P(O)N_3$	88	76	1,4670	1,0504	61,66	61,76
(XVI)	$(Me_2N)_2P(S)N_3$	96	62	1,5188	1,1628	50,42	50,78
(XVII)	$(Et_2N)_2P(S)N_3$	89	84	1,5058	1,0812	69,89	71,25

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* Satisfactory elemental analyses obtained for P.

† The AR value of N_3 is assumed to be 9.61 [11].

EXPERIMENTAL METHOD

IR spectra were taken on a UR-20 instrument. ^{31}P–NMR spectra were obtained on a "Bruker HX-90" instrument under impulse conditions, with high-field suppression of spin–spin interaction between phosphorus nuclei and protons, operating at a frequency of 36.43 MHz (external standard, 85% H_3PO_4). The purity of the compounds obtained was verified by TLC (silufol-250; eluant hexane–acetone, 7 : 3).

Tetraethyldiamidoazidophosphate (XV). A mixture of 45.4 g (0.2 mole) tetraethyldiamidochlorophosphate [9] and 17.6 g (0.27 mole) NaN_3 in 90 ml anhydrous pyridine was stirred at ~20° for 20 h. The pyridine was evaporated under vacuum, 50 ml benzene was added, the precipitated solid was removed by decantation, and the benzene was then evaporated under vacuum. After distillation, 41.0 g (XV) was obtained.

Tetraethyldiamidoazidothiophosphate (XVII). To 26 g (0.4 mole) NaN_3 in 70 ml DMF was added with stirring 48.5 g (0.2 mole) tetraethyldiamidochlorothiophosphate [9]. After addition of the entire quantity of acid chloride, the mixture was stirred at ~20° for 15 min, and then at 60° for 2 h. The reaction mass was mixed with 550 ml cold water and extracted with ether, and the extract was then dried over Na_2SO_4. The ether was evaporated under vacuum; after distillation, 44.4 g (XVII) was obtained.

Triethyl-N-(tetramethyldiamidothiophosphonyl)imidophosphate (VII). To a solution of 5.8 g (0.03 mole) tetramethyldiamidoazidothiophosphate in benzene at 50° was added dropwise 4.86 g (0.036 mole) triethylphosphite. The mixture was kept at 55-60° until nitrogen evolution was complete (10 h). Completion of the reaction was ascertained by disappearance of the band absorption ν_{N_3} of the initial azide from the IR spectrum of the reaction mixture. The benzene was evaporated under vacuum, and 9.1 g (VII) was isolated by distillation.

The other imidophosphates were obtained analogously.

Triphenyl-N-(tetraethyldiamidophosphonyl)phosphinimine (VI). To 3.28 g (0.014 mole) tetraethyldiamidoazidophosphate was added 3.71 g (0.014 mole) triphenylphosphine. The reaction mixture was allowed to stand overnight. The crystalline substance which formed was recrystallized twice from hexane; yield 6.3 g, mp 95°.

CONCLUSIONS

By reaction of phosphites with tetraalkyldiamidoazidophosphates (and –thiophosphates), a series of N-tetraalkyldiamidophosphonyl(and –thiophosphonyl)imidophosphates was obtained.

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