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5-Phosphorylated Furfural and 2-Thiophenecarboxaldehyde Derivatives

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ABSTRACT: *An easy synthetic pathway to 5-phosphorylated furfural and 2-thiophenecarboxaldehyde derivatives has been found, based on their hydrazones.*
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INTRODUCTION

An efficient synthetic method for phosphorylation of five-membered aromatic heterocycles with phosphorus tribromide in basic media that was previously developed by us [1,2] likewise enabled C-phosphorylation of furfural and 2-thiophenecarboxaldehyde hydrazones. Products yielded by the phosphorylation were involved as starting substances in the preparation of 5-phosphorylated furfural and 2-thiophenecarboxaldehyde derivatives. Phosphorylated five-membered heterocycles containing formyl groups at the aromatic ring are regarded as synthetically promising but not easily accessible compounds. So far, this group of organics has been represented by as few as two substances obtained by the reaction of triphenylphosphine with 5-bromo-2-formylthiophene and 5-bromo-2-formylfuran [3]. Here we present a fairly general synthetic access to 5-phosphorylated 2-formylfurans and 2-formylthiophenes.

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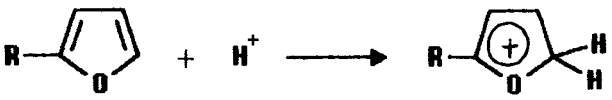
RESULTS AND DISCUSSION

Furfural and 2-thiophenecarboxaldehyde hydrazones are readily phosphorylated with phosphorus tribromide at the position 5 of the heterocyclic ring, the phosphorylation proceeding much faster and under milder conditions than with unsubstituted heterocycles. Dibromophosphines (**1**, **2**) and bromophosphines (**5**, **6**) are indeed formed nearly instantaneously at 5°C on mixing the reagents in the appropriate ratio in pyridine. Running the reaction at elevated temperatures results in a notable amount of polymeric products of undetermined structure. Even tertiary phosphines (**9**, **10**) are formed relatively fast at 20°C in pyridine, whereas neither furan nor thiophene reacts with phosphorus tribromide under the analogous conditions. The orienting effect caused by dimethylhydrazono residues in the course of electrophilic substitutions in five-membered heterocycles was first reported in Refs. [4,5]; however, the data on the electron-donor ability of a hydrazono group are missing in the literature. We attempted to estimate its donor properties by the method presented in Ref. [6], based on ^{13}C NMR spectra. The results provided evidence for a weaker donor ability of the hydrazono group ($\sigma_I = -0.012$, $\sigma_R = -0.058$) than of the methyl group ($\sigma_I = -0.115$, $\sigma_R = -0.181$). In this context, it was expedient to carry out calculations by the MNDO method, with complete geometry optimization, for σ-complexes formed by furan and its derivatives in electrophilic substitution. The data listed in Table 1 suggest that the σ-complex formation requires the least energy

TABLE 1



R=H, Me, Me_2N–N=CH–

Compound	E_{form} for s-complex kcal/mol	E HOMO (eV)
Furan	178.5	−9.143
2-Methylfuran	175.2	−9.032
Furfural hydrazone	156.1	−8.898

(156.1 kcal/mol) for furfural hydrazone, and its highest occupied molecular orbital (HOMO) lies higher (at −8.898 eV) than those of furan and 2-methylfuran.

Thus, the N,N-dimethylhydrazono group in a furan system proves to be more of an electron donor as compared to the methyl group, due to the interaction between the lone electron pair of the nitrogen atom in the amino group and the furan ring.

Dibromophosphines (**1**, **2**) and bromophosphines (**5**, **6**) are stable only in solution, so that on removing the solvent, they convert into polymeric products of undetermined structure. For this reason, they are characterized only by ^{31}P NMR spectra. Tertiary phosphines (**9**, **10**) represent crystalline substances crystallized from heptane that are stable in storage at standard conditions and resistant to atmospheric air (see Table 2).

Notwithstanding the fact that dibromo- and bromophosphines could not be isolated as individual compounds, they allowed a synthetic access to phosphonous diamides (**3**, **4**) and phosphinous amides (**7**, **8**) obtained in high yields, the latter products being rather stable and distillable under reduced pressure without decomposition (see Table 2).

The structures of compounds (**3**, **4**, **7–10**) were corroborated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data (see Tables 3 and 4). ^{13}C NMR spectra unambiguously present evidence for the phosphorylation at position 5 of the heterocycles concerned. Singlet signals in the region δ 7.09–7.48 arising from protons of hydrazono groups in compounds (**3**, **4**, **7–10**) suggest the syn-form for their molecules.

One of the most convenient methods of converting N,N-dimethylhydrazones to aldehydes involves methylation followed by the hydrolysis of the resulting trimethylhydrazonium iodides under mild conditions [7].

Reactions like that are possible for compounds (**3**, **4**, **7–10**) only provided they are first converted into phosphorus(V) derivatives, so as to prevent alkylation at the phosphorus atom. For this purpose, phosphorus(III) derivatives were transformed to oxides (**11**, **12**, **19**, **20**), sulfides (**13**, **14**, **17**, **18**, **21**, **22**), and selenides (**15**, **16**, **23**, **24**). It is notable that oxidized forms of compounds (**7**, **8**) could not be obtained, as the oxidation was accompanied by the cleavage of the P–N bond. The structures of compounds (**11–24**) were supported by ^{1}H, ^{13}C, and ^{31}P NMR spectra (see Table 2–4). Like the trivalent phosphorus derivatives, they exist only in the syn-form.

Alkylation of pentavalent phosphorus derivatives (**11–22**) with an excess of methyl iodide resulted in trimethylhydrazonium iodides (**25–36**); only in the case of running the reaction with tertiary phosphine selenides was an inseparable mixture of N- and Se-alkylated products formed.

Hydrazonium salts (see Table 5) are hygroscopic crystalline substances soluble in acetone and water, with the constitution confirmed by ^{1}H and ^{31}P NMR spectral data (see Tables 5 and 6). ^{1}H NMR spectra for thiophene derivatives exhibit the exocyclic proton signal as two singlets, which may be accounted for by the existence of either syn- and anti-isomers or *cis*- and *trans*-isomers with respect to the partially double C-heterocycle bond. The latter reason appears to be more plausible, as the double signal was likewise observed for 2-thiophenecarboxaldehyde derivatives (**38**, **40–44**).

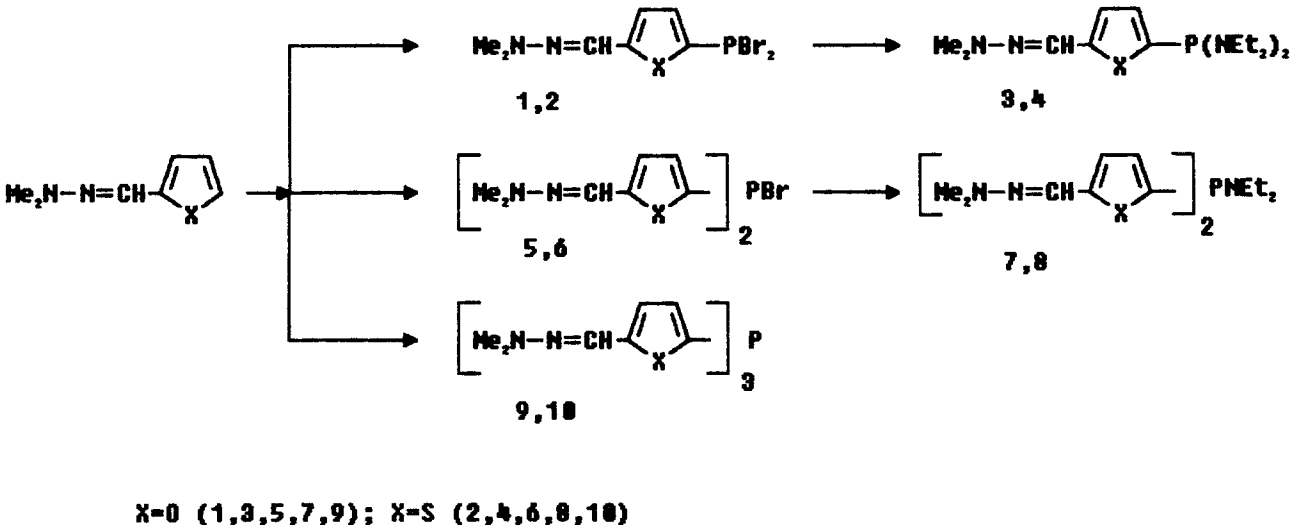
In most instances, the acid hydrolysis of hydrazonium iodides yields phosphorylated aldehydes. Only with compounds (**31**, **32**) are complex mixtures of products are formed. Phosphorylated aldehydes (**37–44**) represent liquids or crystalline solids soluble in the majority of organic solvents; data of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy were consistent with the structures assigned to them (see Tables 5–7).

EXPERIMENTAL

^{31}P, ^{1}H, and ^{13}C NMR spectra were run on a Bruker WP-200 spectrometer using TMS as an internal standard for ^{1}H and ^{13}C signals, and 85% H_3PO_4 as an external standard for ^{31}P signals. All manipulations were carried out in anhydrous solvents.

2-Dimethylhydrazonomethylenefuryl-5-phosphonous Tetraethyldiamide (**3**)

To a stirred solution of phosphorus tribromide (0.1 mol) in benzene (100 mL) at 5°C was added a solution of furfural dimethylhydrazone (0.1 mol) and pyridine (0.1 mol) in benzene (150 mL) over 1 hour.



SCHEME 1

The reaction mixture was warmed for 0.5 hour so that its temperature rose to 20°C. This was followed by the addition of hexane (150 mL) and filtration. To the filtrate was added, with stirring at 5°C over the period of 1 hour, a solution of diethylamine (0.5 mol) in hexane (100 mL). The mixture was warmed to 20°C in 0.5 hour and stirred at this temperature for an additional 2 hours. Then it was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was distilled.

2-Dimethylhydrazonomethylenethienyl-5-phosphonous Tetraethyldiamide (**4**)

To a stirred solution of phosphorus tribromide (0.1 mol) in benzene (75 mL) at 5°C was added a solution of 2-thiophenecarboxaldehyde dimethylhydrazone (0.1 mol) and pyridine (0.1 mol) in benzene (25 mL) over 0.5 hour, which was followed by warming the mixture to 20°C and stirring at this temperature for 5 hours. Then hexane (100 mL) was added, and the precipitate formed was filtered off. To the filtrate was added, with stirring at 5°C over the period of 0.5 hour, a solution of diethylamine (0.45 mol) in hexane (100 mL). After the mixture had been stirred for 15 hours, for it was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was distilled.

Bis(*2-dimethylhydrazonomethylenefuryl-5*)*phosphinous Diethylamide* (**7**)

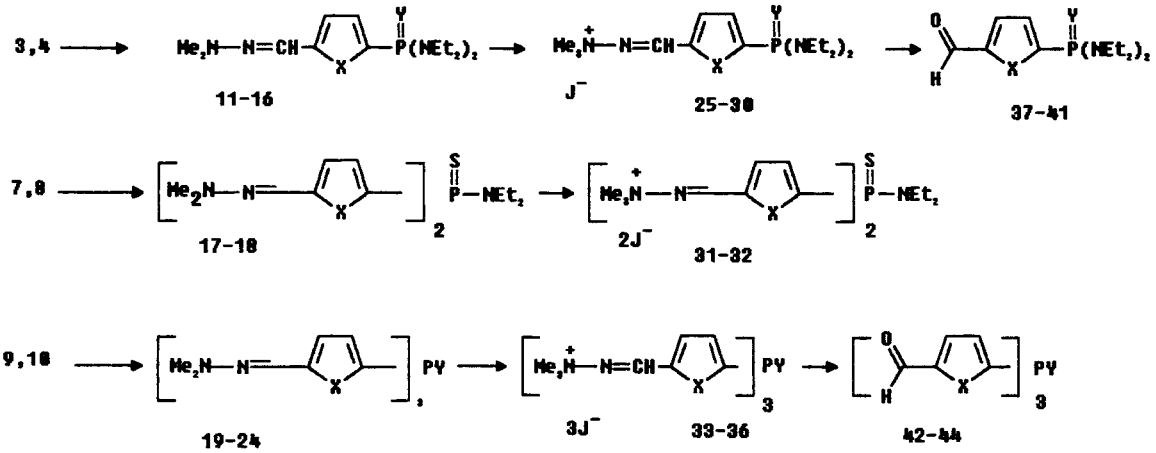
To a stirred solution of phosphorus tribromide (0.1 mol) in benzene (50 mL) at 5°C was added a solution of furfural dimethylhydrazone (0.2 mol) and pyridine (0.25 mol) in benzene (60 mL) over 1 hour. Then the reaction mixture was warmed to 20°C and stirred at this temperature for 24 hours. This was followed by the addition of hexane (50 mL) and filtration. To the filtrate was added, with stirring at 5°C over the period of 0.5 hour, a solution of diethylamine (0.22 mol) in hexane (50 mL). The mixture was warmed to 20°C and stirred at this temperature for 2 hours. Then it was filtered, and the filtrate was evaporated to dryness under reduced pressure. The product was purified by precipitation with hexane from benzene.

Bis(*2-dimethylhydrazonomethylenethienyl-5*)*phosphinous Diethylamide* (**8**)

To a stirred solution of phosphorus tribromide (0.1 mol) in benzene (50 mL) at 5°C was added a solution of furfural dimethylhydrazone (0.2 mol) and pyridine (0.25 mol) in benzene (25 mL) over 1 hour. Then the reaction mixture was stirred for 5 hours and allowed to stand for 45 days. This was followed by the addition of hexane (50 mL) and filtration. To the filtrate was added, with stirring at 5°C over the period of 0.5 hour, a solution of diethylamine (0.22 mol) in hexane (50 mL). The mixture was stirred for 4 hours and left to stand for 12 hours. Then it was filtered, and the filtrate was evaporated to dryness under reduced pressure. The product was purified by precipitation with hexane from benzene.

Tris(*2-dimethylhydrazonomethylenefuryl-5*)*phosphine* (**9**)

To a stirred solution of furfural dimethylhydrazone (0.3 mol) in pyridine (200 mL) at −20°C was added



N	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
X	O	S	O	S	O	S	O	S	O	S	O	S	O	S	O	S	O	S	O
Y	O	O	S	S	Se	Se	S	S	O	O	S	S	Se	Se	O	O	S	S	Se

N	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	
X	S	O	S	O	S	O	S	O	S	O	S	S	O	S	S	
Y	Se	S	S	O	O	S	S	O	O	S	S	Se	S	O	S	

SCHEME 2

TABLE 2 Yields, Analytical Data of **3–24**

No.	Yield, %	BP (°C/0.02 mm) MP, °C	Found, %		Formula	Calcd, %	
			N	P		N	P
3	76	(149–150)	17.84	9.82	$C_{15}H_{29}N_4OP$	17.93	9.91
4	72	(185–187)	16.92	9.24	$C_{15}H_{29}N_4PS$	17.06	9.43
7	67	—	18.24	8.06	$C_{18}H_{28}N_5O_2P$	18.56	8.21
8	71	—	17.57	7.52	$C_{18}H_{28}N_5PS$	18.55	8.21
9	96	108–109	19.04	6.73	$C_{21}H_{27}N_6O_3P$	18.99	7.00
10	98	180–181	17.24	6.13	$C_{21}H_{27}N_6PS_3$	17.13	6.31
11	77	(180–182)	16.92	9.38	$C_{15}H_{29}N_4O_2P$	17.06	9.43
12	95	—	16.03	8.76	$C_{15}H_{29}N_4OPS$	16.27	8.99
13	96	—	16.01	8.64	$C_{15}H_{29}N_4OPS$	16.27	8.99
14	97	—	15.47	8.34	$C_{15}H_{29}N_4PS_2$	15.54	8.59
15	97	—	14.09	7.82	$C_{15}H_{29}N_4OPSe$	14.32	7.91
16	95	83–84	13.57	7.51	$C_{15}H_{29}N_4PSe$	14.93	8.25
17	86	—	16.92	7.21	$C_{18}H_{28}N_5O_2PS$	17.10	7.56
18	92	56–58	16.11	7.18	$C_{17}H_{28}N_5PS_3$	16.30	7.21
19	95	120–121	17.96	6.61	$C_{21}H_{27}N_6O_4P$	18.33	6.76
20	91	195–198	16.41	5.92	$C_{21}H_{27}N_6OPS_3$	16.59	6.11
21	95	188–189	17.52	6.62	$C_{21}H_{27}N_6O_3PS$	17.71	6.53
22	74	218–220	15.97	5.84	$C_{21}H_{27}N_6PS_4$	16.08	5.93
23	96	185–187	15.93	5.81	$C_{21}H_{27}N_6O_3PSe$	16.12	5.94
24	97	225–226	14.52	5.31	$C_{21}H_{27}N_6PS_3Se$	14.76	5.44

TABLE 3 ^{1}H NMR Data of the Compounds **3–24,** δ, (Multiplicity), J(Hz)

			Het								
No.	*Sol*	*δP*	*H_1*	*J_{PH}*	*J_{HH}*	*H_2*	*J_{PH}*	*J_{HH}*	*C–H*	*NMe_2*	*Others*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
3	C_6D_6	80.15	6.472	3.4	3.4	6.385	1.4	3.4	7.124	2.870	3.046–3.096 m (8H, CH_2); 1.070t J_{HH} = 7 (12H, CH_3)
4	C_6D_6	87.53	6.958	2.2	3.6	6.859	1.2	3.6	7.405	2.856	NEt_2 3.00–3.20 m (8H, CH_2); 1.081t J_{HH} = 7.2 (12H, CH_3)
7	C_6D_6	14.92	6.656	1.0	3.4	6.402	—	3.4	7.115	2.889	NEt_2 3.070–3.123 m (4H, CH_2); 0.933t J_{HH} = 6.4 (6H, CH_3)
8	C_6D_6	39.66	7.163	5.0	3.6	7.052	1.6	3.6	7.484	2.951	NEt_2 3.08–3.30 m (4H, CH_2); 1.04–1.19 m (6H, CH_3)
9	C_6D_6	−73.07	6.759	1.2	3.6	6.462	1.0	3.6	7.092	2.935	—
10	C_6D_6	−41.9	7.207	6.6	3.6	6.906	1.4	3.6	7.313	2.913	—
11	$CDCl_3$	15.82	7.020	1.0	3.6	6.505	0.8	3.6	7.075	2.983	NEt_2 3.006–3.215 m (8H, CH_2); 1.075 J_{HH} = 6.6 J_{PH} = 0.8 (12H, CH_3)
12	$CDCl_3$	21.8	7.429	7.6	3.6	6.968	3.6	3.6	7.331	2.957	NEt_2 3.113dq J_{HH} = 7 J_{PH} = 3.2 (8H, CH_2); 1.073t J = 7 (12H, CH_3)
13	$CDCl_3$	59.06	7.144	2.4	3.4	6.467	2.4	3.4	7.040	2.967	NEt_2 3.030–3.330 m (8H, CH_2); 1.068dt J_{HH} = 7 J_{PH} = 1.4 (12H, CH_3)
14	$CDCl_3$	67.3	7.517	8.4	3.4	6.937	3.4	3.4	7.291	2.960	NEt_2 3.176dq J_{HH} = 7 J_{PH} = 5.4 (8H, CH_2); 1.068t J = 7 (12H, CH_3)
15	$CDCl_3$	55.13	7.245	2.8	3.2	6.475	2.4	3.2	7.037	2.992	NEt_2 3.035–3.264 m (8H, CH_2); 1.082t J_{HH} = 7 (12H, CH_3)
16	$CDCl_3$	63.92	7.567	8.8	3.6	6.966	3.6	3.6	7.289	2.968	NEt_2 3.118dq J_{HH} = 7.2 J_{PH} = 5.8 (8H, CH_2); 1.079t J_{HH} = 7.2 (12H, CH_3)
17	$CDCl_3$	32.99	7.122	1.8	3.2	6.533	1.8	3.2	7.346	2.977	NEt_2 3.256–3.02 m (4H, CH_2); 1.044–1.108 m (6H, CH_3)
18	$CDCl_3$	46.74	7.630	9.2	3.6	6.918	2.6	3.6	7.257	2.967	NEt_2 3.057–3.157 m (4H, CH_2); 1.129t J = 6.8 (6H, CH_3)
19	$CDCl_3$	−11.58	7.118	2.0	3.4	6.547	1.8	3.4	7.007	2.943	—
20	$CDCl_3$	6.03	7.486	8.4		6.966	1.8		7.250	2.922	—
21	$CDCl_3$	−5.11	7.122	2.6	3.6	6.559	1.6	3.6	7.043	2.966	—
22	$CDCl_3$	14.18	7.492	9.4	3.8	6.935	2.0	3.8	7.249	2.945	—
23	$CDCl_3$	−21.91	7.134	3.4	3.4	6.545	1.8	3.4	7.021	2.945	—
24	$CDCl_3$	−4.18	7.493	9.6	3.8	6.927	2.2	3.8	7.233	2.937	—

a solution of phosphorus tribromide (0.1 mol) in pyridine (100 mL) over 1 hour. With stirring, the mixture was warmed to 20°C in 4 hours and allowed to stand for 4 hours, which was followed by filtering it and evaporating the filtrate to dryness under reduced pressure. The oily residue was rubbed with water and crystallized from heptane.

Tris(*2-dimethylhydrazonomethylenethienyl-5*)*phosphine* (**10**)

To a stirred solution of 2-thiophenecarboxaldehyde dimethylhydrazone (0.3 mol) in pyridine (150 mL) at 5°C was added a solution of phosphorus tribromide (0.1 mol) in pyridine (50 mL) over 1 hour. The mixture was warmed to 20°C and stirred at this temperature for 50 hours. This was followed by filtering it and evaporating the filtrate to dryness under reduced pressure. The oily residue was rubbed with water and crystallized from benzene/heptane (1/1).

2-Dimethylhydrazonomethylenefuryl-5-phosphonic Tetraethyldiamide (**11**)

To a stirred solution of amide (**3**) (0.1 mol) in hexane (100 mL) at 20°C was added a solution of hexachloroethane (0.1 mol) in hexane (50 mL) over 0.5 hour. Stirring was continued at 20°C for an additional 1 hour, after which hexane was poured off and the oil formed was dissolved in chloroform (100 mL). The

TABLE 4 ^{13}C NMR Data of the Compounds **3–24,** δ, (Multiplicity), J(Hz)

	Het										
	C_1		C_2		C_3		C_4				
No.	δ	J	δ	J	δ	J	δ	J	$C=N$	NMe_2	Others
3	156.3	9.7	118.0	14.5	107.7	—	155.9	5.4	123.1	42.0	NEt_2 42.7d J_{CP} = 17.5 (CH_2); 14.1d J_{CP} = 3.4 (CH_3)
4	144.6	6.5	131.8	14.5	128.9	1.8	147.7	4.2	127.2	43.5	NEt_2 43.1d J_{CP} = 6.4 (CH_2); 15.1d J_{CP} = 3.1 (CH_3)
7	157.0	4.3	120.8	18.2	107.0	3.3	153.8	2.5	122.3	42.1	NEt_2 44.3d J_{CP} = 15.6 (CH_2); 14.0d J_{CP} = (CH_3)
8	140.0	29.9	133.7	25.9	125.0	6.5	147.8	2.0	127.3	41.9	NEt_2 43.4d J_{CP} = 15.7 (CH_2); 13.9d J_{CP} = 3.9 (CH_3)
9	148.4	1.8	123.0	18.2	106.7	4.6	157.8	3.9	123.1	42.6	
10	137.0	21.8	135.8	28.4	125.1	8.7	149.2	—	127.1	42.8	—
11	147.6	196.7	123.2	20.6	105.2	9.5	157.2	8.6	122.0	42.5	NEt_2 38.3d J_{CP} = 5.0 (CH_2); 13.8d J_{CP} = 2.8 (CH_3)
12	131.2	167.2	135.8	9.5	124.2	15.2	149.2	5.3	125.5	42.3	NEt_2 38.1d J_{CP} = 4.4 (CH_2); 13.4d J_{CP} = 3.3 (CH_3)
13	149.6	157.9	124.7	22.9	105.3	8.9	157.5	7.6	121.4	42.4	NEt_2 39.1d J_{CP} = 9.6 (CH_2); 13.4d J_{CP} = 3.4 (CH_3)
14	135.4	132.3	136.6	11.3	124.4	15.0	150.0	5.4	125.8	42.7	NEt_2 39.2d J_{CP} = 4.5 (CH_2); 13.3d J_{CP} = 4.3 (CH_3)
15	149.4	141.1	125.7	24.0	105.4	10.1	157.7	6.7	121.4	42.5	
16	135.3	118.7	137.2	12.0	124.1	15.3	150.2	5.1	125.5	42.6	NEt_2 39.7d J_{CP} = 4.6 (CH_2); 13.1d J_{CP} = 4.3 (CH_3)
17	146.7	148.2	125.2	23.0	105.3	10.0	158.9	7.6	121.4	42.4	NEt_2 39.9d J_{CP} = 7.9 (CH_2); 13.5d J_{CP} = 1.9 (CH_3)
18	133.5	123.1	137.9	12.1	124.1	15.4	151.4	5.3	125.1	42.5	NEt_2d J_{CP} = (CH:i2); d J_{CP} = (CH_3)
19	143.9	160.5	125.6	21.6	105.2	9.3	159.7	8.5	120.5	42.3	
20	131.2	128.0	137.2	10.2	124.4	14.5	152.0	6.1	124.6	42.5	—
21	143.5	135.1	125.3	22.2	105.3	9.8	160.0	7.8	121.2	42.5	
22	133.3	105.0	137.2	11.2	124.5	14.5	152.1	5.5	125.0	42.3	—
23	141.8	124.6	125.8	22.2	105.3	9.4	160.2	7.2	121.3	42.5	NEt_2 39.6d J_{CP} = 5.2 (CH_2); 13.3d J_{CP} = 3.7 (CH_3)
24	132.1	95.2	137.9	11.4	124.5	15.0	152.3	5.2	125.2	42.6	—

TABLE 5 Yields, Analytical Data of 25–44

			Found, %			Calcd, %	
No.	Yield, %	BP (°C/0.02 mm) MP, °C	N	P	Formula	N	P
25	90	46–47	11.72	6.34	$C_{16}H_{32}IN_4O_2P$	11.91	6.59
26	95	45–47	11.39	6.24	$C_{16}H_{32}IN_4OPS$	11.52	6.37
27	95	—	11.44	6.16	$C_{16}H_{32}IN_4OPS$	11.52	6.37
28	95	54–58	11.06	5.95	$C_{16}H_{32}IN_4PS_2$	11.15	6.16
29	87	68–70	10.47	5.63	$C_{16}H_{32}IN_4OPSe$	10.51	5.81
30	85	121–124	10.02	5.78	$C_{16}H_{32}IN_4PSSe$	10.20	5.64
31	87	97–99	10.01	4.17	$C_{20}H_{34}I_2N_5O_2PS$	10.10	4.47
32	84	59–60	9.52	4.24	$C_{20}H_{34}I_2N_5PS_3$	9.65	4.27
33	88	93–95	9.61	3.18	$C_{24}H_{36}I_3N_6O_4P$	9.50	3.50
34	92	137–138	8.92	3.06	$C_{24}H_{36}I_3N_6OPS_3$	9.01	3.32
35	96	85–87	9.11	3.18	$C_{24}H_{36}I_3N_6O_3PS$	9.33	3.44
36	96	154–156	8.71	3.02	$C_{24}H_{36}I_3N_6PS_4$	8.86	3.27
37	74	—	9.53	10.71	$C_{13}H_{23}N_2O_3P$	9.78	10.82
38	81	93–94	9.14	10.17	$C_{13}H_{23}N_2O_2PS$	9.26	10.24
39	77	78–79	8.94	9.98	$C_{13}H_{23}N_2O_2PS$	9.26	10.24
40	84	56–57	8.72	9.52	$C_{13}H_{23}N_2OPS_2$	8.80	9.73
41	68	55–56	7.59	8.32	$C_{13}H_{23}N_2OPSSe$	7.67	8.48
42	69	143–146	8.94[a]	8.61	$C_{15}H_9O_6PS$	9.21	8.89
43	71	156–157	25.17[a]	8.04	$C_{15}H_9O_4PS_3$	25.28	8.14
44	73	142–143	32.08[a]	7.54	$C_{15}H_9O_3PS_4$	32.34	7.81

[a]Analysis for S.

TABLE 6 ^{1}H NMR Data of the Compounds **3–24,** δ, (Multiplicity), J(Hz)

			Het								
No.	*Sol*	*δP*	H_1	J_{PH}	J_{HH}	H_2	J_{PH}	J_{HH}	*C–H*	NMe_2	*Others*
1	2	3	4	5	6	7	8	9	10	11	12
25	CD_3CN	12.35	7.655	—	—	7.175	—	—	9.946	3.935	NEt_2 3.119 (8H, CH_2); 1.128 (12H, CH_3)
26	CD_3CN	19.02	7.517	6.8	3.8	7.949	2.6	3.8	9.543–9.550	3.548	NEt_2 3.060dq J_{HH} = 6.8 J_{PH} = 4 (8H, CH_2) 1.046t J = 6.8 (12H, CH_3)
27	CD_3CN	58.61	7.608	—	—	7.265	—	—	9.815	3.851	NEt_2 3.138 (8H, CH_2); 1.085 (12H, CH_3)
28	CD_3CN	63.92	7.594	7.0	3.8	8.017	2.2	3.8	9.826–9.832	3.660	NEt_2 3.157dq J_{HH} = 7.2 J_{PH} = 5.6 (8H, CH_2); 1.053t J = 7.2 (12H, CH_3)
29	CD_3CN	55.16	7.400	2.0	3.6	7.282	2.0	3.6	9.286	3.586	$NEt_2$3.043–3.393m (8H, CH_2); 1.071t J_{HH} = 7(12H, CH_3)
30	CD_3CN	60.75	7.601	7.0	3.8	7.960	2.0	3.8	9.46–9.469	3.524	NEt_2 3.164ddq J_{HH} = 7 J_{PH} = 6 J = 1.6 (8H, CH_2); 1.064t J_{HH} = 7 (12H, CH_3)
31	CD_3CN	−32.24	7.585–7.624	—	—	7.328–7.384	—	—	9.354–9.362	3.49–3.602	$NEt_2$3.060–3.215m (4H, CH_2); 1.011–1.960m (6H, CH_3)
32	CD_3CN	45.11	7.754	8.0	3.8	7.992	2.4	3.8	9.609–9.6	3.549	NEt_2 3.182dq J_{HH} = 7.2 J_{PH} = 6.9 (4H_2CH_2); 1.948t J_{HH} = 7.2 (6H, CH_3)
33	CD_3CN	−12.81	7.562	1.6	3.6	7.487	2.0	3.6	9.265	3.523–3.552	—
34	CD_3CN	4.86	7.776	8.2	4.0	8.044	2.2	4.0	9.46–9.468	3.477–3.503	—
35	CD_3CN	−5.71–6.31	7.490–7.559		—	—	—	—	9.277	3.521–3.550	—
36	CD_3CN	13.12	7.766	8.8	3.8	8.047	2.0	3.8	9.556–9.565	3.525	—
37	$CDCl_3$	14.77	7.320	1.8	3.2	7.232	1.4	3.2	9.766	—	NEt_2 3.120q J_{HH} = 7.2 (8H, CH_2); 1.091t J_{HH} = 7.2 (12H, CH_3)
38	$CDCl_3$	19.17	7.644	6.8	3.6	7.825	3.6	3.6	9.994–10.004	—	NEt_2 3.118 J_{HH} = 6.8 J_{PH} = 3.8 (8H, CH_2); 1.092t J = 6.8 (12H, CH_3)
39	$CDCl_3$	58.32	7.328	1.8	—	7.328	1.8	—	9.773	—	NEt_2 3.120–3.250m (8H, CH_2); 1.085t J_{HH} = 7.2 (12H, CH_3)
40	$CDCl_3$	65.12	7.698	7.4	3.6	7.818	3.6	3.6	9.981–9.991	—	NEt_2 3.177dq J_{HH} = 7 J_{PH} = 5.6 (8H, CH_2); 1.089t J_{HH} = 7 (12H, CH_3)
41	$CDCl_3$	62.86	7.774	7.6	3.8	7.859	2.4	3.8	9.986–9.998	—	NEt_2 3.201ddq J_{HH} = 7.2 J_{PH} = 5.8 J = 1.8 (8H, CH_2); 1.1t J_{HH} = 7.2 (12H, CH_3)
42	$CDCl_3$	5.56	7.431	2.2	3.6	7.388	1.6	3.6	9.798	—	—
43	$CDCl_3$	3.96	7.708	7.4	3.4	7.865	2.2	3.4	9.965–9.975	—	—
44	$CDCl_3$	13.43	7.756	8.8	3.8	7.52	2.0	3.8	9.983–9.997	—	—

solution was shaken with 5% aqueous sodium bicarbonate $NaHCO_3$ (100 mL). The chloroform layer was dried with sodium sulfate and evaporated to dryness under reduced pressure; the residue was distilled.

2-Dimethylhydrazonomethylenethienyl-5-phosphonic Tetraethyldiamide (**12**)

This was prepared from amide (**4**) by a procedure similar to that for amide (**11**).

2-Dimethylhydrazonomethylenefuryl-5-thiophosphonic Tetraethyldiamide (**13**)

To a stirred solution of amide (**3**) (0.1 mol) in benzene (100 mL), finely divided sulfur (0.1 mol) was strewn, which was followed by stirring the mixture at 20°C for an additional 4 hours. Benzene was evaporated to dryness under reduced pressure to give the product.

TABLE 7 ^{13}C NMR Data of the Compounds **3–24**, δ (Multiplicity), J (Hz)

	Het									
	C_1		C_2		C_3		C_4			
No.	δ	J	δ	J	δ	J	δ	J	$C=O$	Others
37	155.8	185.0	122.7	20.0	120.8	8.8	155.5	7.4	178.6	NEt_2 38.3d J_{CP} = 5.0(CH_2); 13.7d J_{CP} = 2.8 (CH_3)
38	145.2	157.9	136.3	14.3	135.6	9.4	148.7	5.3	183.4	$NEt_2$38,4 d J_{CP} = 4, 4(CH_2); 13,6d J_{CP} = 3,2(CH_3)
39	158.1	145.1	123.8	22.7	120.8	9.5	155.3	6.3	178.6	NEt_2 38.9d J_{CP} = 5.0(CH_2) = 5.0(CH_2); 13.3d J_{CP} = 3.5 (CH_3)
40	149.5	125.0	136.1	14.3	135.3	10.4	148.6	4.9	183.5	NEt_2 39, 1d J_{CP} = 4,4(CH_2); 13,6d J_{CP} = 3,2(CH_3)
41	149.7	110.4	135.9	14.0	135.6	10.9	148.5	4.9	183.6	NEt_2 39,7d J_{CP} = 4,5(CH_2); 13,0d J_{CP} = 4,3(CH_3)
42	149.2	125.6	125.3	22.4	119.7	9.6	157.5	6.9	179.0	—
43	140.8	120.9	136.2	13.8	137.8	10.5	151.3	5.7	183.1	—
44	143.6	97.4	137.4	11.2	136.0	14.6	151.1	4.9	183.1	—

2-Dimethylhydrazonomethylenethienyl-5-thiophosphonic Tetraethyldiamide (**14**)

This was prepared from amide (**4**) similarly to amide (**13**).

2-Dimethylhydrazonomethylenefuryl-5-selenophosphonic Tetraethyldiamide (**15**)

To a solution of amide (**3**) (0.03 mol) in benzene (20 mL), selenium was strewn, and the mixture was stirred under argon for 12 hours. The benzene was evaporated to dryness and the oil was left to stand in vacuo.

2-Dimethylhydrazonomethylenethienyl-5-selenophosphonic Tetraethyldiamide (**16**)

This was prepared similarly to amide (**15**) starting from amide (**4**).

Bis(*2-dimethylhydrazonomethylenefuryl-5*)*thiophosphinic Diethylamide* (**17**)

This was prepared similarly to amide (13) starting from amide (7).

Bis(*2-dimethylhydrazonomethylenethienyl-5*)*thiophosphinic Diethylamide* (**18**)

This was prepared similarly to amide (**13**) starting from amide (**8**).

Tris(*2-dimethylhydrazonomethylenefuryl-5*)*phosphine Oxide* (**19**)

To a stirred solution of phosphine (**9**) (0.2 mol) in chloroform (300 mL) was added 25% hydrogen peroxide (40 mL) over 0.5 hour, and the reaction mixture was boiled with stirring for 3 hours. Then it was neutralized with 20% aqueous sodium hydroxide, and the chloroform layer was separated and dried with sodium sulfate. The chloroform solution was evaporated to dryness under reduced pressure. The product was purified by precipitation with hexane from benzene.

Tris(*2-dimethylhydrazonomethylenethienyl-5*)*phosphine Oxide* (**20**)

This was synthesized analogously to oxide (**19**) from phosphine (**10**) and purified by precipitation with pentane from benzene.

Tris(*2-dimethylhydrazonomethylenefuryl-5*)*phosphine Sulfide* (**21**)

To a stirred solution of phosphine (**9**) (0.02 mol) in benzene (50 mL), sulfur (0.02 mol) was strewn at 50°C, and the mixture was boiled for 2 hours. Then the benzene solution was evaporated to dryness under reduced pressure. The product was crystallized from benzene/hexane (1/5).

Tris(*2-dimethylhydrazonomethylenethienyl-5*)*phosphine Sulfide* (**22**)

The same procedure as for sulfide (**21**) was used starting from phosphine (**10**). The product was purified by precipitation with hexane from benzene.

Tris(*2-dimethylhydrazonomethylenefuryl-5*)*phosphine Selenide* (**23**)

To a solution of phosphine (**9**) (0.05 mol) in benzene (50 mL), selenium (0.05 mol) was strewn, and the

mixture was boiled in a stream of argon for 7 hours. The product was precipitated with hexane from benzene.

Tris(*2-dimethylhydrazonomethylenethienyl-5*)*phosphine Selenide* (**24**)

This was prepared analogously to selenide (**23**) from phosphine (**10**).

2-Trimethylhydrazoniomethylenefuryl-5-phosphonic Tetraethyldiamide Iodide (**25**)

A solution of amide (**11**) (0.1 mol) in methyl iodide (10 mL) was boiled for 10 hours. The methyl iodide solution was evaporated to dryness under reduced pressure. The residual oil was treated with diethyl ether and pentane followed by maintaining it in vacuo.

2-Trimethylhydrazoniomethylenethienyl-5-phosphonic Tetraethyldiamide Iodide (**26**)

This was synthesized from amide (**12**) analogously to salt (**25**).

2-Trimethylhydrazoniomethylenefuryl-5-thiophosphonic Tetraethyldiamide Iodide (**27**)

This was synthesized from amide (**13**) analogously to salt (**25**).

2-Trimethylhydrazoniomethylenethienyl-5-thiophosphonic Tetraethyldiamide Iodide (**28**)

This was synthesized from amide (**14**) analogously to salt (**25**).

2-Trimethylhydrazoniomethylenefuryl-5-selenophosphonic Tetraethyldiamide Iodide (**29**)

A solution of amide (**15**) (0.04 mol) in methyl iodide (30 mL) was boiled for 3 hours. The oily product was precipitated with hexane (50 mL) and then triturated with the same solvent.

2-Trimethylhydrazoniomethylenethienyl-5-selenophosphonic Tetraethyldiamide Iodide (**30**)

This was synthesized from amide (**16**) analogously to salt (**29**).

Bis(*2-trimethylhydrazoniomethylenefuryl-5*)*thiophosphinic Diethylamide Diiodide* (**31**)

This was synthesized from amide (**17**) analogously to salt (**25**) and purified by precipitation with diethyl ether from acetonitrile.

Bis(*2-trimethylhydrazoniomethylenethienyl-5*)*thiophosphinic Diethylamide Diiodide* (**32**)

This was synthesized from amide (**18**) analogously to salt (**25**).

Tris(*2-trimethylhydrazoniomethylenefuryl-5*)*phosphine Oxide Triiodide* (**33**)

A solution of phosphine oxide (**19**) (0.2 mol) in methyl iodide (50 mL) was boiled for 4 hours. The precipitate was filtered off and washed with benzene.

Tris(*2-trimethylhydrazoniomethylenethienyl-5*)*phosphine Oxide Triiodide* (**34**)

This was prepared starting from phosphine oxide (**20**) by the same procedure as salt (**33**).

Tris(*2-trimethylhydrazoniomethylenefuryl-5*)*phosphine Sulfide Triiodide* (**35**)

This was prepared starting from phosphine sulfide (**21**) by the same procedure as salt (**33**).

Tris(*2-trimethylhydrazoniomethylenethienyl-5*)*phosphine Sulfide Triiodide* (**36**)

This was prepared starting from phosphine sulfide (**22**) by the same procedure as salt (**33**).

2-Formylfuryl-5-phosphonic Tetraethyldiamide (**37**)

To a solution of salt (**25**) (0.1 mil) in water (100 mL), hydrochloric acid (0.1 mol) was added, and the mixture was maintained at 70°C for 5 hours. The resulting aldehyde was extracted with diethyl ether (three portions of 150 mL each) and dried with sodium sulfate. Then the ether solution was evaporated, and the residue was extracted with hot hexane. This was followed by freezing the product out by cooling the solution to −40°C.

2-Formylthienyl-5-phosphonic Tetraethyldiamide (**38**)

This was prepared from salt (**26**) similarly to aldehyde (**37**) and crystallized from heptane by freezing out.

2-Formylfuryl-5-thiophosphonic Tetraethyldiamide (**39**)

This was prepared from salt (**27**) similarly to aldehyde (**37**) and crystallized from octane by freezing out.

2-Formylthienyl-5-thiophosphinic Tetraethyldiamide (**40**)

This was prepared from salt (**28**) similarly to aldehyde (**37**) and crystallized from heptane by freezing out.

2-Formylthienyl-5-selenophosphonic Tetraethyldiamide (**41**)

This was prepared from salt (**30**) similarly to aldehyde (**37**) and crystallized from heptane by freezing out.

Tris(*2-formylfuryl-5*)*phosphine Sulfide* (**42**)

To a solution of salt (**35**) (0.2 mol) in water (150 mL), hydrochloric acid (0.6 mol) was added, and the mixture was maintained at 80°C for 5 hours. The resulting precipitate, after being filtered off, was purified by reprecipitation from acetonitrile with diethyl ether.

Tris(*2-formylthienyl-5*)*phosphine Oxide* (**43**)

This was synthesized from salt (**34**) analogously to aldehyde (**42**).

Tris(*2-formylthienyl-5*)*phosphine Sulfide* (**44**)

This was synthesized from salt (**36**) analogously to aldehyde (**42**).

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