C-Phosphorylation of formaldehyde and crotonaldehyde N,N-dimethylhydrazones

*A. A. Tolmachev, A. S. Merkulov, A. A. Yurchenko, M. G. Semenova, and A. M. Pinchuk**

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 5 ul. Murmanskaya, 252660 Kiev, Ukraine. Fax: 380 (044) 543 6843. E-mail: iochkiev@sovamua.com

The first representatives of hydrazones having trivalent phosphorus at the azomethine carbon atom or the carbon atom vinylogous to it were synthesized by reactions of formaldehyde and crotonaldehyde *N,N*-dimethylhydrazones with PBr_3 and diphenylchlorophosphine in the presence of organic bases. Some properties of the compounds synthesized were studied.

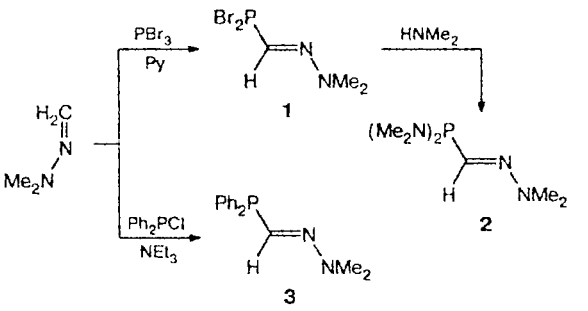
Key words: aldehyde *N,N*-dialkylhydrazones, trivalent phosphorus, phosphorylation.

The paper by M. I. Kabachnik *et al.*[1] reporting on the synthesis of the first representatives of hydrazones containing a phosphoryl group at an azomethine carbon atom gave rise to a new line of research in the chemistry of organophosphorus compounds: the chemistry of *C*-phosphorylated azomethines. Subsequently *C*-phosphorylated hydrazones have been synthesized both by the Kabachnik method[2] and by fundamentally different methods.[3–5] However, all the existing methods for the synthesis of *C*-phosphorylated hydrazones permit preparation of only derivatives of pentavalent phosphorus. Meanwhile, in numerous publications concerning the chemistry of aldehyde *N,N*-dialkylhydrazones, it has been shown that, owing to the conjugation of the lone electron pair of the amine nitrogen atom with the multiple bond, these compounds act not only as N-nucleophiles but also as C-nucleophiles and readily undergo electrophilic substitution at the C atom, for example, formylation[6] and acylation[7]. It can be suggested that phosphorylation of aldehyde *N,N*-dialkylhydrazones with phosphorus trihalides in basic media would enable the synthesis of the corresponding hydrazonoyldihalophosphines and thus make accessible various derivatives containing a P^{III} atom at an azomethine carbon atom. The first results of our studies along this line were published in brief communications.[8,9]

Results and Discussion

We found that formaldehyde *N,N*-dimethylhydrazone is phosphorylated by PBr_3 at the azomethine carbon atom. The reaction occurs under mild conditions (20 °C) in the presence of pyridine as a base (Scheme 1). The resulting hydrazonoyldibromophosphine **1** is stable only in solutions and has been characterized only by ^{31}P NMR spectra (δP 174.5). When compound **1** reacts with an excess of $HNMe_2$, diaminophosphine **2** is formed in good yield. The structure of compound **2** was proved by ^1H and ^{13}C NMR spectra. The presence of the spin-spin coupling of the P atom with the azomethine C atom ($^1J_{PC}$ = 22.3 Hz) and with the proton at this C atom ($^2J_{PH}$ = 28.8 Hz) is especially significant. Formaldehyde *N,N*-dimethylhydrazone can also be phosphorylated by a less reactive phosphorylating reagent, Ph_2PCl, to give tertiary phosphine **3**, which is a low-melting crystalline compound stable to air.

Scheme 1



Phosphorylation of crotonaldehyde *N,N*-dimethylhydrazone involves the C(3) atom and yields compound **4** (Scheme 2). This is the normal reaction route for electrophilic substitution in *N,N*-dimethylhydrazones of α,β-unsaturated aldehydes.[10] Compound **4** polymerizes on attempted isolation; it was characterized only by ^{31}P NMR spectroscopy (δP 175.0) and identified after transformation into more stable ester **5** and amides of the corresponding phosphonous acid **6**.

Due to the lower reactivity of crotonaldehyde *N,N*-dimethylhydrazone, caused by the lengthening of the conjugation chain with the amino group, and to the destabilizing action of the electron-donating methyl group, we

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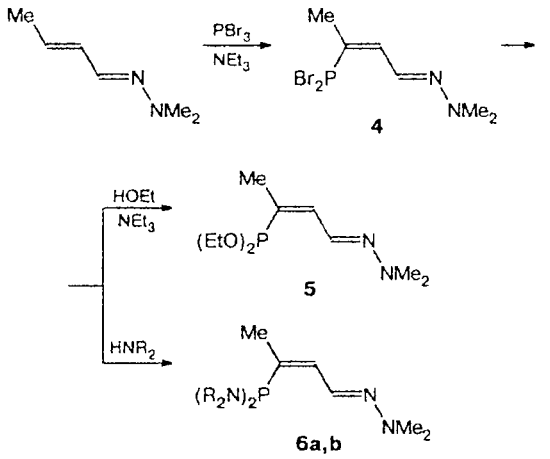
Scheme 2



R = Me (**a**), Et (**b**)

were unable to conduct phosphorylation by less reactive phosphorylating reagents. Thus crotonaldehyde *N,N*-dimethylhydrazone does not react with Ph_2PCl, and its reaction with Ph_2PI gives a complex mixture of nonidentified products.

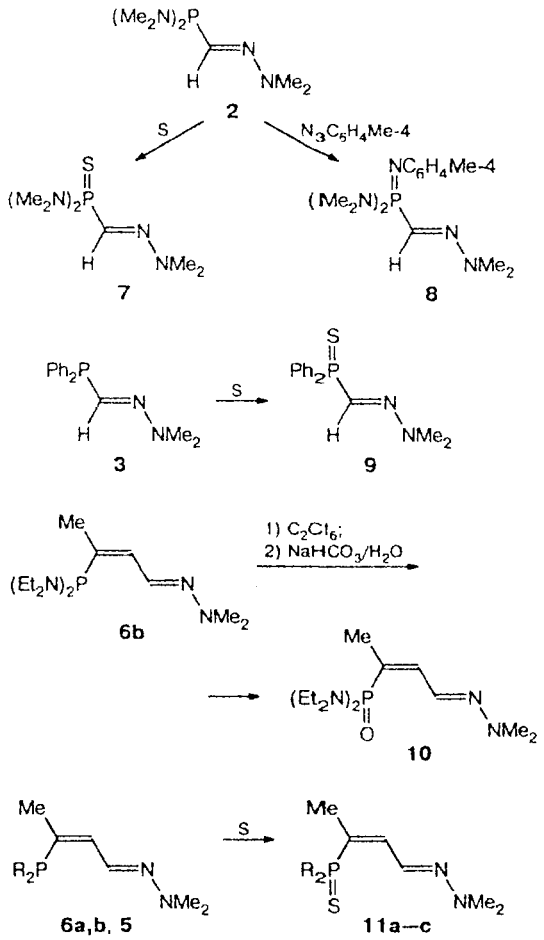
The compounds **1**—**6** synthesized are the first representatives of hydrazones having a P^{III} atom at an azomethine carbon atom or at a carbon atom vinylogous to it. In addition, *C*-phosphorylated formaldehyde *N,N*-dimethylhydrazones can be regarded as derivatives of a previously unknown type of compounds with a formyl group at a trivalent phosphorus atom.

Using traditional methods for increasing the valence, we converted compounds **2**, **3**, **5**, and **6** into derivatives of pentavalent phosphorus **7**—**11** (Scheme 3).

It was found that the reactions of diaminophosphine sulfides **11a,b** and **7** with MeI involve different reaction sites, *viz.*, the N atom of the dimethylamino group in the former case (the reaction affords ammonium salts **12a,b**) and the S atom of the thiophosphoryl group in the latter case (the reaction gives phosphonium salt **13**) (Scheme 4). The different routes of methylation of compounds **11a,b** and **7** are apparently due to the fact that in the former case, the $-I$-effect of the thiophosphoryl group has a lesser influence on the basicity of the dimethylamino group of the hydrazone fragment and to the fact that steric hindrance around the S atom is more significant.

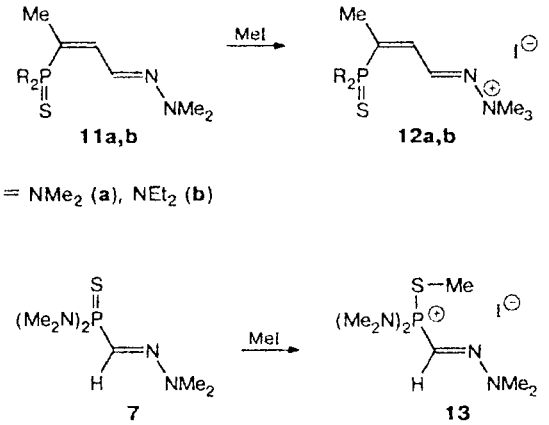
The structure of compound **13** was confirmed, in addition to the ^{31}P NMR spectra, by the presence of signals corresponding to the methyl group at the S atom in the ^1H and ^{13}C NMR spectra: δH 2.48 (d, J_{PH} = 15.2 Hz); δC 12.19 (d, J_{PC} = 3.5 Hz). The dimethylamino group of the hydrazone fragment of salt **13** is exhibited as a broadened singlet at 3.37 ppm in the ^1H NMR spectra and is not manifested at all in the

Scheme 3



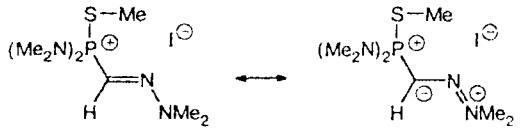
11: R = NMe_2 (**a**), NEt_2 (**b**), OEt (**c**)

Scheme 4



R = NMe_2 (**a**), NEt_2 (**b**)

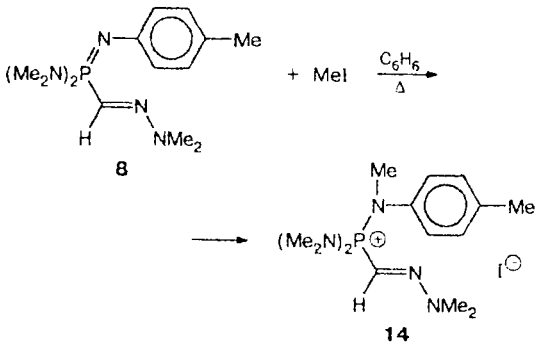
^{13}C NMR spectra. This is probably caused by the presence of a barrier to rotation around the N—N bond arising due to a substantial contribution of the resonance structure **13'** stabilized by the $-I$-effect of the phosphoryl group. Note for comparison that the ^{1}H NMR spectra of ammonium salts **12a,b** contain a narrow singlet in the region of 3.50 ppm, and the ^{13}C NMR spectra contain a signal at 56.2 ppm corresponding to the methyl groups at the ammonium N atom.



13 **13'**

As should be expected, imino phosphonate **8** is also methylated yielding phosphonium salt **14** (Scheme 5).

Scheme 5



8 **14**

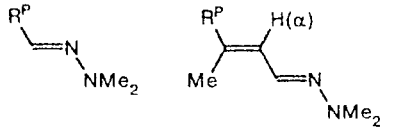
For all phosphorylated hydrazones, *syn—anti*-isomerism is theoretically possible, and for crotonaldehyde hydrazones, *cis—trans*-isomerism is possible as well.

Table 1. Physicochemical constants, ^{31}P NMR spectra, and elemental analysis data for compounds **2**, **3**, and **5—14**

Compound	Yield (%)	B.p./°C (*p*/Torr) [m.p./°C (solvent for crystallization)]	δP (solvent)	Found / Calculated (%) P	Found / Calculated (%) N	Molecular formula
2	50	69—75 (0.08)	84.4 (C_6H_6)	16.45 / 16.28	30.01 / 29.45	$C_7H_{19}N_4P$
3	75	[48—50 (heptane)]	18.1 (C_6H_6)	11.73 / 12.08	10.62 / 10.93	$C_{15}H_{17}N_2P$
5	31	87—90 (0.03)	166.6 (hexane)	13.03 / 13.33	12.27 / 12.06	$C_{10}H_{21}N_2O_2P$
6a	47	105—108 (0.03)	105.6 (hexane)	13.49 / 13.45	23.97 / 24.33	$C_{10}H_{23}N_4P$
6b	52	133—135 (0.04)	102.3 (C_6H_6)	11.13 / 10.81	19.87 / 19.56	$C_{14}H_{31}N_4P$
7	75	[61—64 (hexane)]	71.8 (C_6H_6)	13.62 / 13.93	25.51 / 25.20	$C_7H_{19}N_4PS$
8	59	*	13.6 (CH_2Cl_2)	10.60 / 10.49	23.96 / 23.71	$C_{14}H_{26}N_5P$
9	60	[98—100 (hexane)]	34.8 (C_6H_6)	10.45 / 10.74	9.62 / 9.71	$C_{15}H_{17}N_2PS$
10	48	*	31.7 (CH_2Cl_2)	10.73 / 10.24	18.95 / 18.63	$C_{14}H_{31}N_4OP$
11a	85	*	87.5 (hexane)	11.65 / 11.80	21.12 / 21.37	$C_{10}H_{23}N_4PS$
11b	79	*	82.7 (C_6H_6)	9.53 / 9.72	17.21 / 17.59	$C_{14}H_{31}N_4PS$
11c	66	*	92.6 (C_6H_6)	11.45 / 11.72	10.39 / 10.60	$C_{10}H_{21}N_2O_2PS$
12a	58	[160 (decomp.) (Pr^iOH)]	83.8 (MeOH)	7.63 / 7.66	13.79 / 13.86	$C_{11}H_{26}IN_4PS$
12b	51	*	79.9 (MeCN)	6.50 / 6.73	12.35 / 12.17	$C_{15}H_{34}IN_4PS$
13	43	[85—87 (Pr^iOH)]	51.6 (MeCN)	8.29 / 8.50	15.07 / 15.38	$C_8H_{22}IN_4PS$
14	64	*	41.7 (EtOH)	7.49 / 7.08	16.32 / 16.01	$C_{15}H_{29}IN_5P$

* Oil.

However, according to NMR data, all the phosphorylated hydrazones that we synthesized exist as a single isomer. We suggest that all of them assume the thermodynamically more favorable *E*-configuration at the C=N bond. In the case of crotonaldehyde derivatives, the *trans*-configuration at the C=C bond is realized, as indicated by the magnitudes of the spin-spin coupling constants of the phosphorus atom with the H(α) proton and with the azomethine carbon atom. For example, for compound **10**, these values are 20 and 10.2 Hz, respectively.



(R^P is a P-centered substituent)

Experimental

^{31}P NMR spectra were recorded on a Bruker WP-200 instrument (85% H_3PO_4 as the external standard); ^1H and ^{13}C NMR spectra were measured on a Gemini-200 spectrometer (Me_4Si as the internal standard). Physicochemical characteristics, spectral parameters, and the data of elemental analysis for compounds **2**, **3**, and **5**—**14** are listed in Tables 1 and 2. All the operations with compounds of P^{III} were carried out in an atmosphere of dry argon.

***N,N*-Dimethylhydrazonomethylbis(dimethylamino)phosphine (2).** A solution of PBr_3 (0.01 mol) in 5 mL of pyridine was added with stirring and cooling to 0 °C to a solution of formaldehyde *N,N*-dimethylhydrazone (0.01 mol) in 25 mL of petroleum ether. After 5 h, a solution of $HNMe_2$ (0.05 mol) in 10 mL of petroleum ether was added to the reaction mixture at 0 °C; the precipitate was separated, the filtrate was concentrated, and the residue was distilled.

***N,N*-Dimethylhydrazonomethyl(diphenyl)phosphine (3).** Ph_2PCl (0.01 mol) was added with stirring and cooling to 0 °C to a mixture of formaldehyde *N,N*-dimethylhydrazone

Table 2. ^1H and ^{13}C NMR spectra of compounds **2**, **3**, and **5**—**14**

Compound	Solvent	δH (*J*/Hz)	δC (*J*/Hz)
2	C_6D_6	2.68 (d, 12 H, $PNCH_3$, J_{PH} = 9.4); 2.83 (d, 6 H, $NNCH_3$, J_{HH} = 0.6); 6.71 (dd, 1 H, CH, J_{PH} = 28.8, J_{HH} = 0.6)	41.59 (d, $PNCH_3$, J_{PC} = 14.5); 42.43 (s, $NN(CH_3)_2$); 136.36 (d, CH, J_{PC} = 22.3)
3	C_6D_6	2.94 (s, 6 H, $NNCH_3$); 7.00 (d, 1 H, CH, J_{PH} = 8.6); 7.35 (m, 10 H, Ph)	42.62 (s, CH_3); 128.95 (d, *m*-C(Ph), J_{PC} = 6.2); 129.09 (d, *p*-C(Ph), J_{PC} = 8.2); 132.76 (d, CH, J_{PC} = 9.2); 133.26 (d, *o*-C(Ph), J_{PC} = 18.1); 138.83 (d, *ipso*-C(Ph), J_{PC} = 8.24)
5	CD_3CN	1.25 (t, 6 H, $OCH_2\underline{CH_3}$, J_{HH} = 7.0); 1.90 (d, 3 H, C(β)CH_3, J_{PH} = 8.0); 2.94 (s, 6 H, $NNCH_3$); 3.86 (m, 4 H, OCH_2CH_3); 6.64 (m, 1 H, C(α)H); 7.13 (d, 1 H, CH=N, J_{HH} = 9.4)	11.81 (d, C(β)$\underline{C}H_3$, J_{PC} = 14.5); 17.07 (d, $OCH_2\underline{C}H_3$, J_{PC} = 5.5); 42.45 (s, $NNCH_3$); 62.28 (d, $O\underline{C}H_2CH_3$, J_{PC} = 13.4); 129.77 (d, C(α), J_{PC} = 13.5); 133.89 (d, C(β), J_{PC} = 37.4); 138.07 (d, CH=N, J_{PC} = 19.6)
6a	CD_3CN	1.80 (dd, 3 H, CCH_3, J_{PH} = 8.4, J_{HH} = 1.4); 2.67 (d, 12 H, $PNCH_3$, J_{PH} = 9.0); 2.85 (s, 6 H, $NNCH_3$); 6.21 (m, 1 H, C(α)H); 7.22 (d, 1 H, CH=N, J_{HH} = 9.4)	14.0 (d, $C\underline{C}H_3$, J_{PC} = 23.3); 41.97 (d, $PNCH_3$, J_{PC} = 15.3); 42.95 (s, $NNCH_3$); 132.16 (d, C(β), J_{PC} = 14.9); 132.62 (d, C(α), J_{PC} = 4.3); 136.67 (s, CH=N)
6b	CD_3CN	1.05 (t, 12 H, $NCH_2\underline{CH_3}$, J_{HH} = 7.2); 1.80 (d, 3 H, CCH_3, J_{PH} = 8.4, J_{HH} = 1.4); 2.83 (s, 6 H, $NNCH_3$); 3.01 (dq, 8 H, NCH_2CH_3, J_{PH} = 9.5, J_{HH} = 7.2); 6.28 (m, 1 H, C(α)H); 7.20 (d, 1 H, CH=N, J_{HH} = 9.4)	13.86 (d, C(β)$\underline{C}H_3$, J_{PC} = 23.5); 14.29 (d, $NCH_2\underline{C}H_3$, J_{PC} = 3.0); 42.24 (s, $NNCH_3$); 42.94 (d, $N\underline{C}H_2CH_3$, J_{PC} = 16.0); 130.73 (d, C(β), J_{PC} = 15.9); 132.19 (d, C(α), J_{PC} = 3.6); 137.04 (d, CH=N, J_{PC} = 3.0)
7	$CDCl_3$	2.66 (d, 12 H, $PNCH_3$, J_{PH} = 12.0); 3.03 (s, 6 H, $NNCH_3$); 6.40 (d, 1 H, CH=N, J_{PH} = 46.8)	36.77 (d, $PNCH_3$, J_{PC} = 2.76); 41.95 (s, $NNCH_3$); 123.28 (d, CH=N, J_{PC} = 168.5)
8	CD_3OD	2.19 (s, 3 H, 4-$C\underline{H_3}C_6H_4$); 2.69 (d, 12 H, $PNCH_3$, J_{PH} = 9.9); 3.00 (s, 6 H, $NNCH_3$); 6.41 (d, 1 H, CH=N, J_{PH} = 42.0); 6.74 (d, 2 H, *m*-H(Ph), J_{HH} = 9.6); 6.88 (d, 2 H, *o*-H(Ph), J_{HH} = 9.6)	
9	$CDCl_3$	3.04 (s, 6 H, $NNCH_3$); 6.69 (d, 1 H, CH=N, J_{PH} = 43.8); 7.45 (m, 6 H, *m*-H(Ph), *p*-H(Ph)); 7.87 (m, 4 H, *o*-H(Ph))	42.45 (s, $NNCH_3$); 121.75 (d, CH=N, J_{PC} = 159.45); 128.60 (d, *m*-C(Ph), J_{PC} = 12.6); 131.54 (d, *p*-C(Ph), J_{PC} = 2.9); 132.42 (d, *o*-C(Ph), J_{PC} = 10.7); 133.84 (d, *ipso*-C(Ph), J_{PC} = 87.0)
10	$CDCl_3$	1.11 (t, 12 H, $NCH_2\underline{CH_3}$, J_{HH} = 7.0); 1.97 (dd, 3 H, C(β)CH_3, J_{PH} = 13.4, J_{HH} = 1.4); 3.01 (s, 6 H, $NNCH_3$); 3.07 (m, 8 H, NCH_2CH_3); 6.78 (m, 1 H, C(α)H); 7.16 (d, 1 H, CH=N, J_{HH} = 9.6)	13.96 (d, $NCH_2\underline{C}H_3$, J_{PC} = 2.9); 13.97 (d, C(β)$\underline{C}H_3$, J_{PC} = 16.4); 38.52 (d, $N\underline{C}H_2CH_3$, J_{PC} = 4.4); 42.66 (s, $NNCH_3$); 126.84 (d, C(β), J_{PC} = 153.16); 130.24 (d, C(α), J_{PC} = 23.6); 137.55 (d, CH=N, J_{PC} = 10.6)

(to be continued)

Table 2 (*continued*)

Compound	Solvent	δH (*J*/Hz)	δC (*J*/Hz)
11a	$CDCl_3$	2.03 (d, 3 H, C(β)CH_3, J_{PH} = 14.0); 2.63 (d, 12 H, $PNCH_3$, J_{PH} = 11.6); 3.02 (s, 6 H, $NNCH_3$); 6.89 (m, 1 H, C(α)H); 7.03 (d, 1 H, CH=N, J_{HH} = 9.6)	13.82 (d, C(β)$\underline{C}H_3$, J_{PC} = 12.1); 37.00 (d, $PNCH_3$, J_{PC} = 3.1); 42.49 (s, $NNCH_3$); 125.40 (d, C(β), J_{PC} = 123.0); 128.29 (d, C(α), J_{PC} = 22.8); 137.21 (d, CH=N, J_{PC} = 10.5)
11b	$CDCl_3$	1.11 (t, 12 H, $NCH_2\underline{C}H_3$, J_{HH} = 7.0); 2.01 (d, 3 H, C(β)CH_3, J_{PH} = 15.6); 2.99 (s, 6 H, $NNCH_3$); 3.14 (m, 8 H, $NC\underline{H}_2CH_3$); 6.77 (m, 1 H, C(α)H); 7.00 (d, 1 H, CH=N, J_{HH} = 9.4)	14.15 (d, $NCH_2\underline{C}H_3$, J_{PC} = 3.4); 14.65 (d, C(β)$\underline{C}H_3$, J_{PC} = 13.6); 39.90 (d, $N\underline{C}H_2CH_3$, J_{PC} = 4.5); 42.96 (s, $NNCH_3$); 128.19 (d, C(β), J_{PC} = 123.8); 129.41 (d, C(α), J_{PC} = 22.8); 136.07 (d, CH=N, J_{PC} = 9.9)
11c	$CDCl_3$	1.31 (t, 6 H, $OCH_2\underline{C}H_3$, J_{HH} = 7.0); 1.99 (d, 3 H, C(β)CH_3, J_{PH} = 15.4); 3.02 (s, 6 H, $NNCH_3$); 4.08 (m, 4 H, $OC\underline{H}_2CH_3$); 7.02 (m, 1 H, C(α)H); 7.20 (d, 1 H, CH=N, J_{HH} = 9.4)	12.59 (d, C(β)$\underline{C}H_3$, J_{PC} = 10.3); 16.12 (d, $OCH_2\underline{C}H_3$, J_{PC} = 7.3); 42.42 (s, $NNCH_3$); 62.29 (d, $O\underline{C}H_2CH_3$, J_{PC} = 5.8); 125.08 (d, C(β), J_{PC} = 123.4); 127.03 (d, C(α), J_{PC} = 27.4); 139.42 (d, CH=N, J_{PC} = 15.7)
12a[a]	CD_3CN	2.28 (dd, 3 H, C(β)CH_3, J_{PH} = 14.4, J_{HH} = 1.5); 2.63 (d, 12 H, $PNCH_3$, J_{PH} = 11.7); 3.53 (s, 9 H, $NNCH_3$); 6.97 (m, 1 H, C(α)H); 8.92 (d, 1 H, CH=N, J_{HH} = 9.3)	15.20 (d, C(β)$\underline{C}H_3$, J_{PC} = 8.2); 36.27 (d, $PNCH_3$, J_{PC} = 3.1); 55.44 (s, $NNCH_3$); 130.14 (d, C(α), J_{PC} = 13.6); 155.45 (d, C(β), J_{PC} = 111.0); 161.03 (d, CH=N, J_{PC} = 22.2)
12b	CD_3CN	1.11 (t, 12 H, $NCH_2\underline{C}H_3$, J_{HH} = 7.0); 1.97 (dd, 3 H, C(β)CH_3, J_{PH} = 14.6, J_{HH} = 1.4); 3.11 (m, 8 H, $NC\underline{H}_2CH_3$); 3.51 (s, 9 H, $NNCH_3$); 6.81 (m, 1 H, C(α)H); 8.82 (d, 1 H, CH=N, J_{HH} = 9.4)	13.45 (d, $NCH_2\underline{C}H_3$, J_{PC} = 3.2); 16.92 (d, C(β)$\underline{C}H_3$, J_{PC} = 8.0); 39.26 (d, $N\underline{C}H_2CH_3$, J_{PC} = 4.2); 56.16 (s, $NNCH_3$); 128.33 (d, C(α), J_{PC} = 13.2); 154.86 (d, C(β), J_{PC} = 110.8); 161.63 (d, CH=N, J_{PC} = 22.0)
13[b]	CD_3CN	2.48 (d, 3 H, SCH_3, J_{PH} = 15.2); 2.93 (d, 12 H, $PNCH_3$, J_{PH} = 11.4); 3.37 (s, 6 H, $NNCH_3$); 7.01 (d, 1 H, CH=N, J_{PH} = 54.2)	12.19 (d, SMe, J_{PC} = 3.5); 37.95 (d, $PNCH_3$, J_{PC} = 3.0); 107.62 (d, CH=N, J_{PC} = 183.1)
14	CD_3OD	2.36 (s, 3 H, 4-$C\underline{H}_3C_6H_4$); 2.72 (d, 12 H, $PNCH_3$, J_{PH} = 10.2); 3.15 (d, 3 H, $\underline{H}_3CNC_6H_4CH_3$-4, J_{PH} = 8.8); 3.20 (s, 6 H, $NNCH_3$); 6.30 (d, 1 H, CH=N, J_{PH} = 48.0); 7.16 (s, 4 H, *o*-H(Ph), *m*-H(Ph))	

[a] The ^1H NMR spectrum was recorded in methanol-d_4.
[b] The ^1H NMR spectrum was recorded in $CDCl_3$.

(0.01 mol), NEt_3 (0.02 mol), and 25 mL of pyridine, and the mixture was allowed to stand for ~48 h at 20 °C. The precipitate that formed was separated, and the filtrate was diluted with 25 mL of benzene and filtered. The solvents were evaporated, and the residue was recrystallized.

4-(*N,N*-Dimethylhydrazono)but-2-en-2-yl(diethoxy)phosphine (5). A solution of PBr_3 (0.01 mol) in 20 mL of petroleum ether was added dropwise with stirring and cooling to 0 °C to a mixture of crotonaldehyde *N,N*-dimethylhydrazone (0.01 mol), NEt_3 (0.02 mol), and 60 mL of petroleum ether, and the mixture was allowed to stand for 12 h. Then anhydrous EtOH (0.05 mol) was added with stirring and cooling to −5 °C. After 3 h, the precipitate was filtered off, the solvent was evaporated, and the residue was distilled *in vacuo*.

4-(*N,N*-Dimethylhydrazono)but-2-en-2-ylbis(dimethylamino)phosphine (6a). A solution of PBr_3 (0.01 mol) in 20 mL of heptane was added dropwise with stirring and cooling to 0 °C to a mixture of crotonaldehyde hydrazone (0.01 mol), NEt_3 (0.02 mol), and 60 mL of petroleum ether, and the mixture was allowed to stand for 12 h. Then $HNMe_2$ (0.05 mol) was added with stirring and cooling to −5 °C. After 2 h, the precipitate was filtered off, the solvent was evaporated, and the residue was distilled *in vacuo*.

4-(*N,N*-Dimethylhydrazono)but-2-en-2-ylbis(diethylamino)phosphine (6b) was prepared similarly to compound **6a**.

***N,N*-Dimethylhydrazonomethylbis(dimethylamino)phosphine sulfide (7).** Finely powdered sulfur (0.01 mol) was added to a solution of compound **2** (0.01 mol) in 40 mL of benzene, and the mixture was allowed to stand for ~24 h at 20 °C. The solvent was evaporated *in vacuo*, and the residue was recrystallized.

***N,N*-Dimethylhydrazonomethyl-*N*-(*p*-tolyl)phosphonimidic acid bis(*N,N*-dimethylamide) (8).** *p*-Tolylazide (0.01 mol) was added to a solution of compound **2** (0.01 mol) in 40 mL of benzene, the mixture was refluxed for 2 h, the solvent was evaporated, and the product was reprecipitated from benzene by petroleum ether. The oil was dried *in vacuo*.

***N,N*-Dimethylhydrazonomethyl(diphenyl)phosphine sulfide (9).** Finely powdered sulfur (0.01 mol) was added to a solution of compound **3** (0.01 mol) in 40 mL of benzene, the mixture was refluxed for 3 h, the solvent was evaporated, and the residue was recrystallized.

4-(*N,N*-Dimethylhydrazono)but-2-en-2-ylbis(diethylamino)phosphine oxide (10). A solution of C_2Cl_6 (0.01 mol) in 20 mL of heptane was added to a solution of compound **6b** (0.01 mol) in 40 mL of heptane. The resulting oil was separated, washed with 20 mL of heptane, and dissolved in 20 mL of $CHCl_3$. The solution was shaken with a saturated aqueous solution of $NaHCO_3$. The organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was evaporated, and the oil was dried *in vacuo*.

4-(*N,N*-Dimethylhydrazono)but-2-en-2-ylbis(dimethylamino)phosphine sulfide (11a). Finely powdered sulfur (0.01 mol) was added to a solution of compound **6a** (0.01 mol) in 40 mL of heptane. After 3 h, the resulting oil was separated, washed with 5 mL of heptane, and dried *in vacuo*.

4-(*N,N*-Dimethylhydrazono)but-2-en-2-ylbis(diethylamino)phosphine sulfide (11b) was prepared similarly to compound **11a**.

Diethyl 4-(*N,N*-dimethylhydrazono)but-2-en-2-ylphosphonothioate (11c). Finely powdered sulfur (0.01 mol) was added to a solution of compound **5** (0.01 mol) in 40 mL of benzene, and the mixture was refluxed for 3 h. Heptane (60 mL) was added, and the oil formed was dried *in vacuo*.

***N*'-{3-[Bis(dimethylamino)thiophosphoryl]but-2-enylidene}-*N,N,N*-trimethylhydrazinium iodide (12a).** Methyl iodide (0.03 mol) was added to a solution of compound **11a** (0.01 mol) in 30 mL of benzene, and the mixture was refluxed for 6 h. After cooling the reaction mixture to room temperature, 30 mL of Et_2O was added, and the resulting precipitate was separated and recrystallized.

***N*'-{3-[Bis(diethylamino)thiophosphoryl]but-2-enylidene}-*N,N,N*-trimethylhydrazinium iodide (12b)** was prepared similarly to compound **12a**.

***N,N*-Dimethylhydrazonomethylbis(dimethylamino)(methylthio)phosphonium iodide (13).** Methyl iodide (0.02 mol) was added to a solution of compound **7** (0.01 mol) in 40 mL of benzene, and the mixture was allowed to stand for 6 h at 20 °C. The product was precipitated from a benzene solution with Et_2O, filtered off, and recrystallized.

***N,N*-Dimethylhydrazonomethylbis(dimethylamino)(methyl-4-tolylamino)phosphonium iodide (14).** A mixture of compound **8** (0.01 mol) and MeI (0.02 mol) in 40 mL of benzene was refluxed for 4 h. The resulting oil was separated, washed with benzene (2×20 mL), and dried *in vacuo*.

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