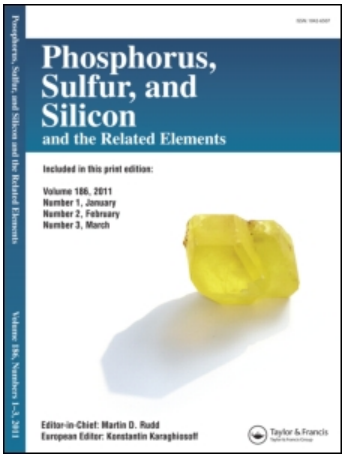


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOSPHORYLATION OF ENAMINEHYDRAZONES AS AN EFFICIENT ROUTE TO DIAZAPHOSPHOLINES AND DIAZAPHOSPHOLES

Andrey A. Tolmachev[a]; Sergey I. Dovgopoly[a]; Aleksandr N. Kostyuk[a]; Igor V. Komarov[a]; Aleksandr M. Pinchuk[a]
[a] Institute of Organic Chemistry of National Academy of Science of Ukraine, Kiev, Ukraine

To cite this Article Tolmachev, Andrey A. , Dovgopoly, Sergey I. , Kostyuk, Aleksandr N. , Komarov, Igor V. and Pinchuk, Aleksandr M.(1997) 'PHOSPHORYLATION OF ENAMINEHYDRAZONES AS AN EFFICIENT ROUTE TO DIAZAPHOSPHOLINES AND DIAZAPHOSPHOLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 123: 1, 125 — 140
To link to this Article: DOI: 10.1080/10426509708044203
URL: http://dx.doi.org/10.1080/10426509708044203

Phosphorus, Sulfur, and Silicon, 1997, Vol. 123, pp. 125-140
Reprints available directly from the publisher
Photocopying permitted by license only

PHOSPHORYLATION OF ENAMINEHYDRAZONES AS AN EFFICIENT ROUTE TO DIAZAPHOSPHOLINES AND DIAZAPHOSPHOLES*

ANDREY A. TOLMACHEV†, SERGEY I. DOVGOPOLY, ALEKSANDR N. KOSTYUK, IGOR V. KOMAROV and ALEKSANDR M. PINCHUK

Institute of Organic Chemistry of National Academy of Science of Ukraine, Murmanskaya 5, Kiev 252094, Ukraine

(Received 21 October 1996; In final form 14 January 1997)

1,2,3-diazaphospholines of new type containing an enamine residue, conjugated with the diazaphospholine cycle, were synthesized by phosphorylation of N,N-dimethyl- and N-substituted hydrazones of ω-formyl-1,3,3-trimethyl-2-methyleneindolines using phosphorus(III) halides. Reversible ionization of the P-Br bond was observed for a 2-N-methyl-3-P-bromodiazaphospholine in polar solvents. The ionization is caused by stabilization of the phosphenium ion by electrondonating methyl and enamine group. Analogously, 2-N-phenyl-3-P-bromo- as well as 3-P-chloro-1,2,3-diazaphospholines give stable phosphenium ions only after treatment of sodium tetraphenylborate or trimethylsilyl trifluoromethanesulfonate.

Keywords: diazaphospholine; phosphorus tribromide; ionization; hydrazones

INTRODUCTION

Previously, we have studied the phosphorylation of enamines and found that enamines of reduced reactivity, for example 1,3,3-trimethyl-2-methyleneindoline, undergo phosphorylation most readily [1]. It has also been reported that 1,3,3-trimethyl-2-methyleneindoline can react twice with some electrophiles at its methylene group. The examples include formylation [2], acylation [3] by carbonic acid anhydrides, halides and isocyanates [4]. We believe that the phospho-

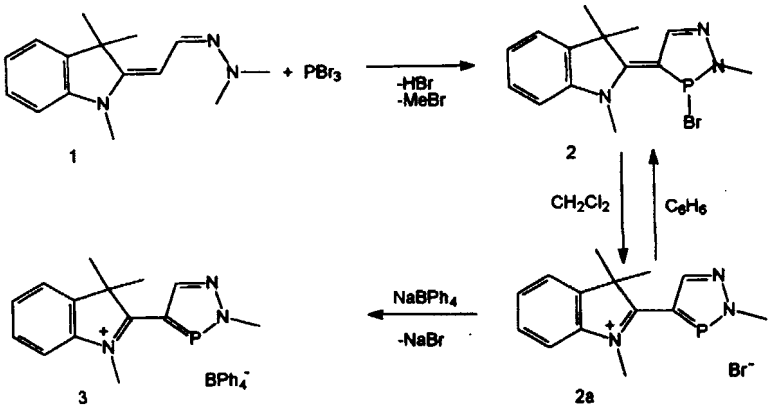
* Dedicated to Professor Robert Wolf on the occassion of his 70th birthday

† To whom correspondence should be addressed.

rylation of enamines by phosphorus(III) halides most closely resembles the above reactions. It might be expected that dimethylhydrazone of ω-formyl-1,3,3-trimethyl-2-methyleneindoline can be phosphorylated at the methylene group by phosphorus(III) halides.

RESULTS AND DISCUSSION

In fact, ω-formyl-1,3,3-trimethyl-2-methyleneindoline dimethylhydrazone **1** reacts with phosphorus tribromide, however it turned out that the reaction proceeds through the hydrazone group with the formation of diazaphospholine cycle. The phosphorylation at the methylene carbon atom by phosphorus tribromide is accompained by demethylation that leads to the diazaphospholine **2**. The reaction was completed within seconds at 20°C in pyridine solution. (see Scheme 1)

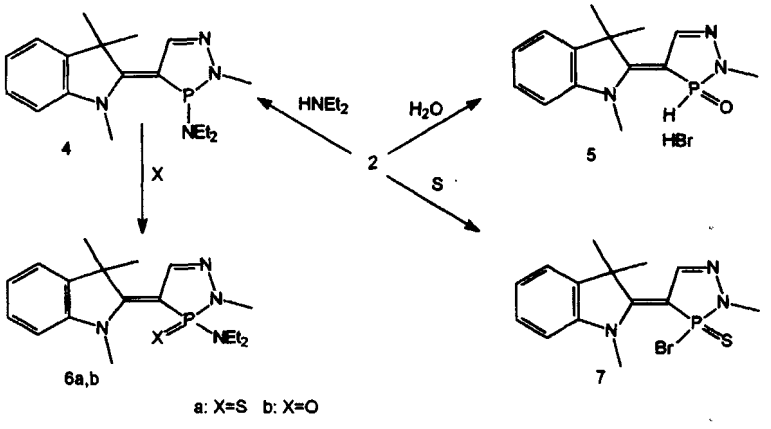


1 2 3 2a

SCHEME 1

^{31}P-NMR spectrum of the diazaphospholine **2** in benzene contains one peak at 160 ppm. A low-field shift of the signal was observed when the spectrum was recorded in dichloromethane or acetonitrile (225 ppm). An intermediate value 192 ppm was obtained for the ^{31}P-NMR chemical shift of **2** in pyridine. ^{31}P-NMR spectra of the bromide **2a** and tetraphenylborate **3** in dichloromethane are identical. From the results obtained it may be deduced that the diazaphospholine **2** exists either in covalent or in ionic form depending on the solvent. There are several literature examples for similar equilibrium between P(III) and phosphenium cations for some P-Hal compounds containing strong electron donating groups[5]. The ionization of P-Hal bond in diazaphospholenes was also reported [6].

The diazaphospholine **2** enters into many reactions which are common for P-Hal derivatives. It reacts with diethylamine to give the amide **4**, and can be hydrolyzed to a hydrophosphoryl derivative **5**. The amide **4** is an unstable compound which was characterized by ^{31}P-NMR spectroscopy and transformed into the phosphonates **6a,b**. Like other halogenophosphines having the electron donating 2-methyleneindoline group [1], **2** reacts readily with sulfur to form the corresponding P=S derivative **7**. (see Scheme 2)

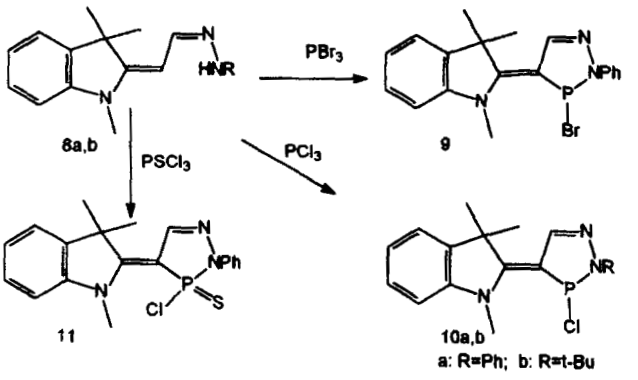


SCHEME 2

Attempts at the phosphorylation of **1** by other phosphorylating reagents - PCl_3, $PhPCl_2$, $POCl_3$, $PSCl_3$, $PSBr_3$ - failed, in our hands, no individual compound was isolated from the reaction mixtures.

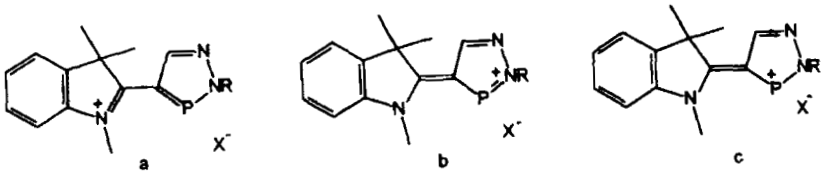
In the case of N-substituted hydrazones of ω-formyl-1,3,3-trimethyl-2-methyleneindoline **8a,b** the cyclization reactions are expected to proceed easier, because it should go through the elimination of HHal, not through the dealkylation. Indeed, starting from **8a,b**, the corresponding diazaphospholines were obtained using not only PBr_3, but also PCl_3, $PSCl_3$ as well (compounds **9-11**). (see Scheme 3) There is some resemblance of these reactions with the well-known Shvetsov-Shilovski hydrazone cyclization [7].

^{31}P-NMR spectra of **9** measured in various solvents (benzene, acetonirtrile, pyridine) are practically identical (δ=152 ppm), unlike those for **2**. Obviously, the diazaphospholine **9** does not give ionic compounds with a two-coordinated phosphorus atom in polar solvents, probably due to the electron withdrawing properties of the phenyl substituent. Ionization of the P-Cl bond in **10b** has not been detected in any solvent; judging from its ^{31}P-NMR spectra, **10b** exists in solutions exclusively in covalent form.



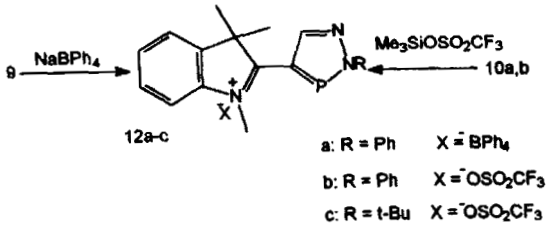
SCHEME 3

Compounds **2** and **3**, as well as **12a-c** (see below) can be described by superposition of at least three resonance structures. As the N-substituent in the diazaphospholine cycle (methyl or phenyl) is crucial for the ionization process, we believe that the contribution of the structure (**b**) with the positively charged nitrogen atom is significant. (see Scheme 4)



SCHEME 4

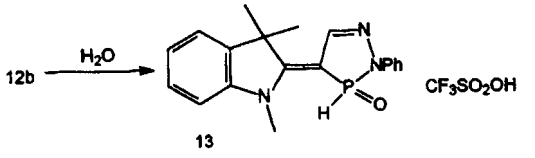
Ionization of **9** and chlorophosphines **10a,b** to **12a-c** occurs readily under treatment of sodium tetraphenylborate or trimethylsilyl trifluoromethanesulfonate. (see Scheme 5)



SCHEME 5

Substances **12a,b** give completely identical ^{31}P-NMR spectra.

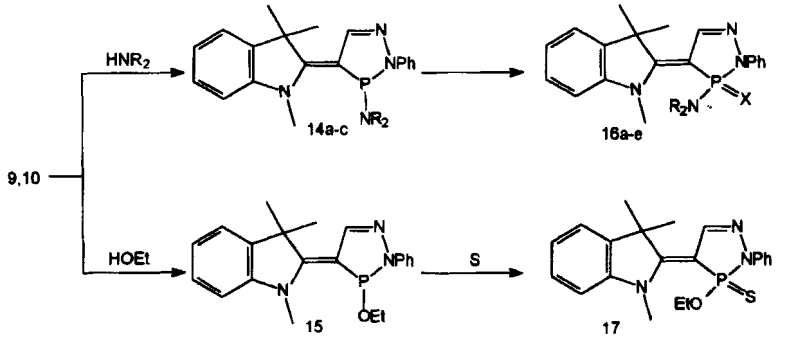
Contrary to **2a, 3** diazaphospholes **12a,b,c** are not susceptible to oxidation by air oxygen and their shelf-life is unlimited. Compound **12b** was transformed into the corresponding derivative **13** under treatment of equimolar amount of water. We failed to separate the diazaphosphole 12c in individual form. (see Scheme 6)



SCHEME 6

Starting from **9, 10a** modified diazaphospholines **14-17** have been synthesized using simple chemical transformations.

Compounds with trivalent phosphorus have been characterized by ^{31}P-NMR spectroscopy and transformed into the corresponding phosphonates **16, 17**. (see Scheme 7)



14a-c a: R = Et; b: -R–R- = -$(CH_2)_2$-O-$(CH_2)_2$-; c: -R–R- = -$(CH_2)_5$-

16 a: R = Et; b: -R–R- = -$(CH_2)_2$-O-$(CH_2)_2$-; c: -R–R- = -$(CH_2)_5$-
X = S; X = S; X = S

d: -R-R- = -$(CH_2)_2$-O-$(CH_2)_2$-; e: -R-R- = -$(CH_2)_2$-O-$(CH_2)_2$-
X = O; X = N-Ph

SCHEME 7

Structures of all the synthesized compounds were proven, with ^{31}P-NMR (Table I), also by elemental analysis (Table II), ^{1}H-NMR spectroscopy (Tables III, IV) and for some key compounds ^{13}C-NMR spectra were recorded (Table V).

TABLE I ^{31}P NMR spectra of substances 2-17 δ_P, ppm, (J_{PH}, Hz)

1	*Solvent*	*δ, ppm*	*1*	*Solvent*	*δ, ppm*
2	$CDCl_3$,CH_2Cl_2	223.2	12b	CH_2Cl_2	233.5
2	C_5H_5N	192.0	12c	$CHCl_3$	233.0
2	C_6H_6	157.0	13	$CHCl_3$	6.0 (548)
3	CH_2Cl_2	242.7	14a	C_5H_5N	56.0
4	C_5H_5N	63.0	14b	C_5H_5N	55.6,55.3
5	C_5H_5N	11.7(560)	14c	C_5H_5N	56.0
6a	C_5H_5N	67.5	15	C_5H_5N	77.3,76.3
6b	CH_2Cl_2	27.4	16a	C_5H_5N	61.0
7	C_5H_5N	60.4	16b	C_5H_5N	60.7,58.5
9	C_5H_5N	153.0	16c	C_6H_6	61.0
10a	C_5H_5N	119.0	16d	C_6H_6	22.0
10b	C_5H_5N	147.0	16e	C_6H_6	9.8
10b	CH_2Cl_2	168.0	17	CH_2Cl_2	69.4
11	C_5H_5N	60.5			
12a	CH_2Cl_2	232.5			

TABLE II Yields analytical data and melting points of substances 1-17

Sub-stance	*Melting point (°C)*	*Yield %*	*Formula*	*Found*		*(Calculated) %*
				C	*H*	*N*
1	126-128	79	$C_{13}H_{21}N_3$	75.2(75,52)	7.81(7.96)	19.09(19.52)
2	179-182 decomp.	62	$C_{14}H_{17}BrN_3P$	49.84(49.72)	5.48(5.07)	12.74(12.42)
8b	oil	78	$C_{17}H_{25}N_3$	74.9(75,17)	9.35(9.28)	15,12(15.55)
				N		P
3	154-157	53	$C_{38}H_{37}BN_3P$	7.01(7.28)		5.14(5.36)
5	181-183	81	$C_{14}H_{19}BrN_3OP$	11.42(11.80)		9.11(8.7)
6a	164-166	31	$C_{18}H_{27}N_4PS$	15.69(15.46)		8.66(8.55)
6b	154-156	30	$C_{18}H_{27}N_4OP$	16.1(16.23)		8.56(8.93)
7	174-176	43	$C_{14}H_{17}BrN_3PS$	11.84(11.35)		8.25(8.36)
9	171-175 decomp.	66	$C_{19}H_{19}BrN_3P$	10.81(10.5)		7.76(7.74)
10a	167-170	68	$C_{19}H_{19}ClN_3P$	11.49(11.81)		8.54(8.71)
10b	178-180	57	$C_{17}H_{23}ClN_3P$	12.23(12.51)		9.01(9.22)

TABLE II Yields analytical data and melting points of substances 1-17 (Continued)

Substance	*Melting point (°C)*	*Yield %*	*Formula*	Found	(Calculated) %
				N	P
11	150-161 decomp.	33	$C_{19}H_{10}ClN_3PS$	10.91(10.83)	7.76(7.98)
12a	145-148	74	$C_{43}H_{39}BN_3P$	6.44(6.57)	4.60(4.84)
12b	138-140	57	$C_{20}H_{19}F_3N_3O_3PS$	8.74(8.95)	6.71(6.60)
13	126-128	56	$C_{20}H_{21}F_3N_3O_4PS$	8.44(8.62)	6.12(635)
16a	172-174	63	$C_{23}H_{29}N_4PS$	13.11(13.20)	7.65(7.30)
16b	176-178	49	$C_{23}H_{27}N_4OPS$	12.87(12.78)	7.11(7.06)
16c	177-178	62	$C_{24}H_{29}N_4PS$	12.54(12.83)	7.42(7.09)
16d	149-150	35	$C_{23}H_{27}N_4O_2P$	12.89(13.26)	7.01(7.36)
16e	138-140	87	$C_{27}H_{32}N_5OP$	14.34(14.07)	5.99(6.22)
17	175-177	51	$C_{21}H_{24}N_3OPS$	10.81(10.57)	7.7(7.79)

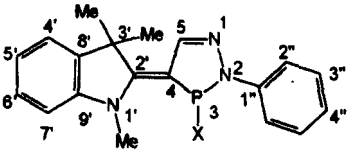
TABLE III PMR spectra of substances 1-3,6,7 ($\delta_H(CDCl_3)$, ppm.; J, Hz)

1	*C3-Me2*	*-P-NMe*	*-NMe*	*-CH=N-*	*Aromatic and other groups*
1	1.6s	--	3.1s	7.8,d	2.8 (6H,s,-NMe),
				JHH=10.0	5.4 (1H,d,=CH-,JHH=-10.0)
					6.5-7.7 (4H,m,Ar)
2	1.8s	4.1,d	4.4,d	8.7,d	7.4-7.7 (4H,m,Ar)
		JPH=11.5	JPH=4.6	JPH=2	
3	1.5s	4.0,d	2.5,d	8.4,d	6.7-7.4 (24H,m,Ar,BPh4)
		JPH=9.5	JPH=3.4	JPH=2.2	
5	1.7s	3.2,d	3.6,d	8.6,d	7.0-7.6 (4H,m,Ar)
		JPH=10	JPH=5.1	JPH=2.1	7.6 (1H,d,P(O)H, JPH=560)
6a	1.6s	3.1,d	3.9s	7.8,d	6.9 (1H,d,H7,JHH=8.0)
		JPH=8.6		JPH=15.4	7.1-7.4 (3H,m,Ar)
					1.1 (6H,t,-CH3(NEt2),JHH=7)
					2.9-3.1,3.2-3.5
					(4H,m,-CH2-(NEt2))
6b	1.5s	3.6,d	4.1s	8.0,d	7.1-7.4(4H,m,Ar)
		JPH=9.1		JPH=13.2	1.1(6H,t,-CH3(NEt2))
					3.0-3.3 (4H,m,-CH2-(NEt2))
7	1.6,s;1.7,s	4.0,d	3.3,d	8.0,d	6.7-7.4 (4H,m,Ar)
		J_{PH}=15.5	J_{PH}=2.8	J_{PH}=15	

TABLE IV PMR spectra of substances 8-15,18,19 ($\delta_H(CDCl_3)$, ppm.; J, Hz)

1	*C3-Me2*	*-NMe*	*o-Ph*	*-CH=N-*	*Aromatic and other groups*
9	1.8s	4.2,d	7.9,d	8.5,d	7.3-7.5 (7H,m,Ar, m,p-Ph)
		J_{PH}=8.0	J_{HH}=8.1	J_{PH}=2.2	
10a	1.7s	4.0,d	7.7,d	8.2,d	7.0-7.4 (7H,m,Ar, m,p-Ph)
		J_{PH}=6.4	J_{HH} =8.0	J_{PH}=2.4	
11	1.7s,1.6s	4.2,S	7.8,d	8.1,d	7.1-7.5 (7H,m,Ar, m,p-Ph)
			J_{HH}=8	J_{PH}=16.8	
8b	1.5s	3.1s,3.2s	---	5.4,d	1.3,1.2(9H,s,-CMe_3)
				J_{HH}=10	4.5 (1H,s,=N-NH-)
					6.6-7.4 (4H,m,Ar)
10b	1.8s	4.3d	--	8.6s	1.7 (9H,s,-Me_3)
		J_{PH}=4			7.3-7.5 (4H,m,Ar)
12a	1.7s	4.2s	7.8,d	8.8d	7.3-7.8 (27H,m,Ar)
			J_{HH}=4.2	J_{PH}=3·0	
12b	1.7s	4.2s	7.8,d	9.0d	7.3-7.8 (7H,m,Ar,m,p-Ph)
			J_{HH}=4	J_{PH}=2.8	
13	1.7s	3.6s	--	6.2d	7.0-7.6 (9H,m,Ar,Ph)
				J_{PH}=3	7.5 (1H,d,P(O)H, J_{PH}=548
16a	1.68s,1.69s	3,9s	7.7,d	8.0d	0.9 (6H,t, -CH_3(NEt_3))
			J_{HH}=8	J_{PH}=16	3.2 (4H,t,-CH_2-(NEt_3))
					6.7-7.3 (7H,m,Ar, m,p-Ph)
16b	1.67s,1,7s	3.9s	7.7,d	8.0d	3.3 (8H,m,-$(CH_2)_2$-0-$(CH_2)_2$-)
			J_{HH}=8	J_{PH}=16	6.9-7.4 (7H,m,Ar, m,p-Ph)
16c	1.66s,1.68s	3.9s	7.7,d	8.0d	1.5 (6H,m,-$(CH_2)_3$-)
			J_{HH}=8	J_{PH}=16	3.2 (4H,s,-N$(CH_2)_2$-)
16d	1.67s,1.69s	3.8s	7.6,d	8.0d	3.3 (8H,m,-$(CH_2)_2$-0-$(CH_2)_2$-)
			J_{HH}=8	J_{PH}=16	6.9-7.4 (7H,m,Ar, m,p-Ph)
16e	1.5s,1.7s	3.8s	7.6,d	8.0d	3.3 (8H,m,-$(CH_2)_2$-0-$(CH_2)_2$-)
			J_{HH}=8	J_{PH}=16	6.6-7.4 (12H,m,Ar, m,p-Ph)
17	1.69s,1.7s	4.0s	7.7,d	8,1d	1.3 (3H,t,-CH_3(OEt))
			J_{HH}=6	J_{PH}=14	3.8 (2H,q,-CH_2-(OEt))
					6.9-7.3 (7H,m,Ar,m,p-Ph)

TABLE V ^{13}C NMR spectra of substances 1,2a,6à,10a,10b,12b δ_C(CDCl3), (Jpc,Hz.)

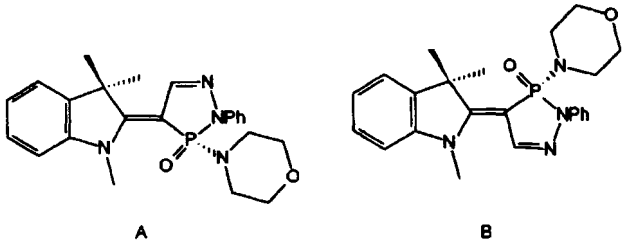


1	*Me_2*	*NMe*	*$C^{3'}$*	*$C^{7'}$*	*C^{4}*	*$C^{5'}$*	*$C^{4'}$*	*$C^{6'}$*	*C^{5}*	*$C^{8'}$*	*$C^{9'}$*	*$C^{2'}$*	*Other atoms*
1	28.8	29.2	45.4	105.9	--	119.5	121.7	128	139	138	145	158	44.6
									(1.5)			(17)	$NNMe_2$ 94.2 =CH-
2a	26.2	41.3	53,2	113.9	124.6	122.6	128.4	129	141.4	142	145	181	36.8
	26.3	(17)	(1.8)		(275)				(1.5)			(17)	19.9 PNMe
6a	27.3,	34.4	49.7	108.7	118.2	121.5	122.8	128.1	138.9	140	144	168	14.0
	28.0		(11)		(229)				(24)			(6.6)	1.7 CH_3NEt_2 39.3 (4.9) CH_2NEt_2 31.9 10.3 PNMe
10a	28.1	33.9	50.3	109.6	108.3	121.9	123.5	128.3	143	140	144	171	118.4,$C^{2"}$
	27.9	27.5	(1.7)		(40)				(38)			(27)	124.3,$C^{4"}$ 129.0,$C^{3"}$ 143.3,$C^{1"}$
10b	27.16	35.9	52.1	112.4	112.3	122.3	126.9	129	144.4	141	143	178	30.2
	27.11	24.1			(42)							(19)	9.9 Me,-t-Bu 61.4 4.5 -C-,-t-Bu
12b	24.8	37.3	54.6	115.5	120.3	129.1	128	130	146.9	--	142	184	121.2,$C^{2"}$
	24.9	(10)			(321)				(1.1)			(20)	(10) 122.7,$C^{4"}$ 129.6,$C^{3"}$1 42,$C^{1"}$

The most characteristic feature of the ^{1}H-NMR spectra is the signal at δ 8.0-8.7 which is attributed to the azomethyne proton (-CH=N-). This peak is shifted mostly to low field for the compounds with two-coordinated phosphorus atom (**2, 3, 12**), which is an additional proof of their ionic nature. The value of $^3J_{P-H}$ in

2, 3, 12(3 Hz) is in the range observed for the compounds with two-coordinated phosphorus. The value of 14-17 Hz has been reported for the analogous coupling constant in compounds with tetracoordinated phosphorus atom [1,8]. Diastereotopic 3-methyl groups of the indoline cycle in all compounds possesing pentavalent phosphorus atom give two ^{1}H-NMR signals. Interestingly, N-methyl group in the diazaphospholines with trivalent phosphorus appears also as two signals. It can be attributed to different conformational isomers. A considerable increase of $^1J_{P\text{-}C}$ in the ^{13}C-NMR spectra can be noted going from the compounds with P(III) (40 Hz) to the substances with tetra (230 Hz) and, especially, two-coordinated phosphorus (~275-320 Hz).

Finally, one can suggest two isomers for the diazaphospholine synthesized (A and B), like for 2-methylene-phosphorylated [8] and other 2-methylene-substituted indolines [9,10]. However, no sign of the isomerism has been noted in the ^{31}P, ^{13}C, ^{1}H-NMR spectra of the investigated compounds.



SCHEME 8

The choice between the isomers in favor of A was made based on Lanthanide Induced Shifts (LIS), caused by Eu(fod)$_3$ in ^{1}H-NMR spectra of **16d** in deuterochloroform. Specific LIS values (extrapolated to the equimolar amounts of Eu(fod)$_3$ and the substrate) are shown on the Figure 1.

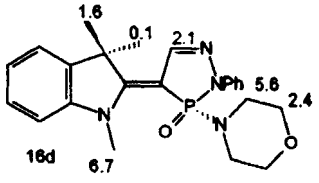


FIGURE 1

There are several possible coordination sites in **16d**, but we believe that the Eu(fod)$_3$ coordination in this case occurs at the P=O group exclusively. This has been postulated based on the literature data [11], and on the fact that the LIS values for the corresponding P=S compound are very small (see Figure 2).

We calculated the structures of Eu(fod)$_3$-**16d** adducts for two possible isomers of **16d** - A and B. The calculations were performed on the assumption of the pseudo-contact nature of LIS (McConnel-Robertson equation). The best fit between calculated and observed LIS was obtained for the structure A.

Analysis of the Eu(fod)$_3$-induced LIS values for the derivative **16e** and for the P=S compound **16b** allows us to make the following conclusions. The preferred Eu(fod)$_3$ coordination site in **16e** is the nitrogen atom of the phenylmino group (see Figure 2). The isomer showed on the Figure 2 should most probably be chosen for the structure of **16e**, for its relative LIS values are close to those of **16e**. The Eu(fod)$_3$ coordination to the P=S compound **16b** occurs through a nitrogen atom of the diazaphospholine cycle, because the LIS values for 3-methyl groups of the indoline cycle are identical. Contrary to **16d** and **16e**, LIS for CH proton of the diazaphospholine cycle in **16b** is larger than the corresponding values for the N-methyl group. It is possible only for the structure **16b** showed on the Figure 2., the shift reagent coordination being occurred at N-atom marked with an arrow.

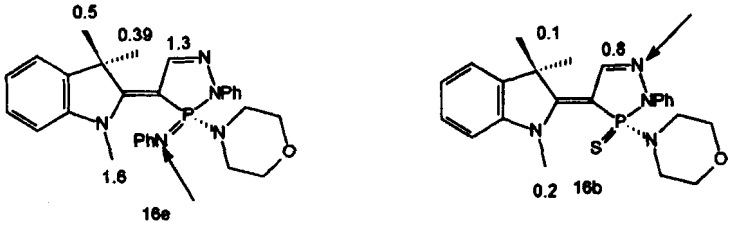


FIGURE 2 The Eu(fod)$_3$ coordination sites are marked with arrows

EXPERIMENTAL

General. NMR spectra were recorded on a Varian-300 instrument TMS was used as an internal standard for ^{1}H and ^{13}C-NMR spectra, 85% H_3PO_4 was an external standard for ^{31}P-NMR measurements. Melting points were measured on a hot stage and are uncorrected. Microanalyses were performed at Microanalytical Laboratory of Institute of Organic Chemistry of National Academy of Science of Ukraine. Eu(fod)$_3$-induced shifts were obtained using the "LSR-titration technique". Atomic coordinates of **16d** for computer calculations were obtained using the PC MODEL program. [11]. The yields and melting points are summarized in Table 2.

1,3,3-Trimethyl-2-methyleneindoline-w-formyl dimethylhydrazone 1

To a solution of Fischer's aldehyde (0.15 mole) in methanol (200 mL), N,N-dimethylhydrazine (0.16 mole) was added. The reaction mixture was refluxed for ca. 3 hours. After removal of the solvent, the residue was distilled.

3-Bromo-2-methyl-4-(1',3',3'-trimethylindoline-2-ylidene)-Δ^5-1,2,3-diazaphospholine 2

To a solution of hydrazone 1 (0.019 mole) in pyridine (25 mL) cooled to 0 °C, a solution of phosphorus tribromide (0.019 mole) in pyridine (5 mL) was added dropwise with stirring, then triethylamine (0.021 mole) was added. The reaction mixture was diluted with benzene (40 mL). The precipitated solid was filtered off, and the solvents were evaporated. The product was purified by reprecipitation with benzene from pyridine.

1,3,3-trimethyl-2-(2'-methyl-2'H-1',2',3'- diazaphosphol-4'-yl)3H-indolium tetraphenylborate 3

To a solution of diazaphospholine 2 (2.7 mmole) in acetonitrile (15 mL) solution of sodium tetraphenylborate (2.7 mmole) in acetonytrile (10 mL) was added. The reaction mixture was stirred at 70 °C for 4 hours. The precipitated solid was filtered off, washed with dichloromethane. The solvents were evaporated. The residue was triturated with petroleum ether. The product was filtered and dried.

2-methyl-3-hydro-3-oxo-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3-Δ^5-diazaphospholine hydrobromide 5

To a solution of diazaphospholine 2 (0.01 mole) in pyridine (30 mL), water (0.01 mole) was added. After 2 hours the solvent was evaporated. The product was purified by reprecipitation with hexane from chloroform

3-Diethylamino-2-methyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)-Δ^5-1,2,3 diazaphospholine 6a

To the reaction mixture of diazaphospholine 2 (7 mmole) in pyridine (20 mL) prepared as described above, diethylamine (0.02 mole) was added. Then a finely ground sulfur (7 mmole) was added. The reaction mixture was stirred for 3 hours till sulfur dissolved. The reaction mixture was diluted with hexane (25 mL). The precipitated solid was filtered off. The solvents were evaporated. The residue was triturated with petroleum ether. The product was recrystallized from n-octane.

3-Diethylamino-2-methyl-3-oxo-4-(1',3',3'-trimethylindoline-2'-ylidene)-Δ^5-1,2,3 diazaphospholine 6b

To the reaction mixture of diazaphospholine 2 (7 mmole) in pyridine(20 mL) prepared as described above, diethylamine (0.02 mole) was added. Then 0.01 mole of 20% $H_2O_2$was added. The reaction mixture was diluted with hexane (25 mL), the precipitated solid was filtered off. The solvents were evaporated. The residue was triturated with petroleum ether. The product was recrystallized from n-octane.

3-Bromo-2-methyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3-Δ^5-diazaphospholine 7.

To a solution of diazaphospholine 2 (0.01 mole) in pyridine (30 mL), a finely ground sulfur was added. The reaction mixture was stirred for ca. 3 hours till sulfur dissolved. The solvent was evaporated. The product was purified by reprecipitation with petroleum ether from benzene.

1,3,3-Trimethyl-2-methyleneindoline-w-formyl phenylhydrazone 8a

It was prepared according to method given in [12].

1,3,3-Trimethyl-2-methyleneindoline-w-formyl tert-butylhydrazone 8b

To a solution of Fischer's aldehyde (0.12 mole) in methanol (150 mL), tert-butylhydrazine (0.13 mole) was added. The reaction mixture was left for 3 hours. After removal of the solvent, the residue was crystallized from heptane.

3-Bromo-2-phenyl-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3-Δ^5-diazaphospholine 9

To a solution of hydrazone 8a (8.7 mmole) in pyridine (20 mL) cooled to 0°C, a solution of phosphorus tribromide (8.7 mmole) in pyridine (10 mL) was added dropwise with stirring, then triethylamine (0.021 mole) was added. The reaction mixture was diluted with benzene (40 mL). The precipitated solid was filtered off, and the solvents were evaporated. The product was purified by reprecipitation with hexane from benzene.

3-Chloro-2-phenyl-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3- Δ^5 -diazaphospholine 10a

To a solution of hydrazone 8a (0.01 mole) in pyridine (25 mL) with cooling to 0°C and stirring a solution of phosphorus trichloride (0.01 mole) in pyridine (10

mL) was added. Then triethylamine (0.03 mole) was added. After 0.5 hour the reaction mixture was diluted with benzene (40 mL). The precipitated solid was filtered off. The solvents were evaporated. The product was purified by reprecipitation with heptane from benzene.

3-Chloro-2-tert.-butyl-4-(1',3',3'-trimethylindoline-2'-ylidene-1,2,3-Δ^5-diazaphospholine 10b

The product was prepared according to the procedure applied to 10a.

3-Chloro-2-phenyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)-Δ^5-1,2,3-diazaphospholine 11.

To a solution of hydrazone 8a (0.01 mole) in pyridine (30 mL) a solution of thiophosphoryl chloride (0.01 mole) in pyridine (10 mL) was added with stirring. After 3 days the reaction mixture was diluted with benzene (45 mL). The precipitated solid was filtered off. The solvents were evaporated. The product was purified by reprecipitation with heptane from benzene.

1,3,3-trimethyl-2-(2'-phenyl-2'H-1',2',3'-diazaphosphol-4'-yl)-3H-indolium tetraphenylborate 12a

To a solution of diazaphospholine 9 (0.01 mole) in dichloromethane (20 mL) a solution of $NaBPh_4$ (0.01 mole) in dichloromethane (20 mL) was added. After 5 hours the solvents were evaporated. The product was recrystallized from benzene.

1,3,3-trimethyl-2-(2'-phenyl-2'H-1',2',3'-diazaphosphol-4'-yl)-3H-indolium trifluoromethanesulfonate 12b

To a solution of diazaphospholine 10a (5 mmole) in dichloromethane trimethylsilyl trifluoromethanesulfonate (5 mmole) was added. After 1 hour the solvent was evaporated. The residue was triturated with petroleum ether, filtered and dried.

Reaction of chlorophospholine 10b with trimethylsilyl trifluoromethanesulfonate.

To a solution of chlorophospholine 10b (5 mmole) in dichloromethane (10 mL) a solution of trimethylsilyl trifluoromethane sulfonate (5 mmole) in dichloromethane (5 mL) was added. ^{31}P spectrum was recorded δ = 233 ppm.

2-Phenyl-3-hydro-3-oxo-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3-diaza phospholine trifluoromethanesulfonate 13.

The salt 12b was left on air for 3 hours. The salt 13 formed was purified by reprecipitation with petroleum ether from methanol.

3-Diethylamino-2-phenyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2, 3-Δ^5-diazaphospholine 16a

To the reaction mixture of diazaphospholine 10a (10 mmole) in pyridine (40 mL) prepared as described above, diethylamine (30 mmole) was added. After 0.5 hour a finely ground sulfur (10 mmole) was added. The reaction mixture was vigorously stirred for 3 hours till sulfur dissolved. The reaction mixture was diluted with hexane (45 mL). The precipitated solid was filtered off. The solvents were evaporated. The residue was triturated with hexane. The product was recrystallized from n-decane.

3-Morpholino-2-phenyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3 - diazaphospholine 16b.

16b was prepared according to the procedure applied to 16a. Product was crystallized from n-decane.

3-Piperidino-2-phenyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)-1,2,3-Δ^5-diazaphospholine 16c.

16c was prepared according to the procedure applied to **16a**. Product was crystallized from n-decane.

3-Morpholino-2-phenyl-3-oxo-4-(1',3',3'-trimethylindoline-2'-ylidene)1,2,3-Δ^5-diazaphospholine 16d.

16d was prepared according to the procedure applied to **6b**. Product was crystallized from n-decane.

3-Morpholino-2-phenyl-3-phenylimino-4-(1',3',3'-trimethylindoline-2'-ylide ne)-1,2,3-Δ^5-diazaphospholine 16e.

To the reaction mixture of bromodiazaphospholine 9 (0.01 mole) in pyridine (40 mL) prepared as described above diethylamine (0.03 mole) was added. After 0.5 hour phenylazide was added. The reaction mixture was diluted with hexane (45 mL). The solid was filtered off. The solvents were evaporated. The product was crystallized from n-decane.

3-Ethoxy-2-phenyl-3-thio-4-(1',3',3'-trimethylindoline-2'-ylidene)- 1,2,3-Δ^5-diazaphospholine 17.

To the reaction mixture of bromophospholine 9 (0.01 mole) in pyridine (40 mL) prepared as described above a mixture of ethanol (0.01 mole) and triethylamine (0.03 mole), then finely ground sulfur was added. The reaction mixture was vigoursly stirred till sulfur dissolved. The reaction mixute was diluted with hexane (45 mL), the precipitated solid was filtered off, the solvents were evaporated. The product was crystallized from n-decane.

Acknowledgements

The partial financial support of this work by DuPont de Nemours & Co., Inc. is gratefully acknowledged.

References

[1] Tolmachev A.A., Kostyuk A.N., Kozlov E.S., Zh.Obsch.Khimii, 1991, Vol. 61, N.6, P. 1333-1341.
[2] Wesch O., Ger.Patent 1.139.121. (November.-8.-1962)
[3] Bailey A.S., Haxby J.B., Hilton A.N.,Peach J.M., Vandrevala M.H.,J.Chem. Soc. Perkin Trans. Part I.-1981-N 2.-P.382-389.
[4] Ivanova Zh. M., Michailik S.K., Shokol V.A.,Derkach G.I., Zh.Obsch. Khimii, 1969, Vol. 39, N 7, P.1504-1511.
[5] Jochem G., Breitsameter F., Schier A., Schmidpeter A., Heteroatom Chemistry, vol.7, N.4, ,1996, P.239-247.
[6] Kibardin A.M., Gryaznova T.V., Sarvarova N.N., Yermolaeva L.V., Vulfson S.G., Pudovik A.N. Doklady Akad. Nauk (Russia) 1992 Vol. 324, N.2, P.330-332.
[7] Shvetsov-Shilovsky N.N., Bobkova R.G., Ignatova N.P., Melnikov N.N. Uspechi Khimii, 1977, Vol.46, P.967.
[8] Tolmachev A.A., Kostyuk A.N., Kozlov E.S., Pinchuk A.M. Zh.Obsch.Khimii, 1990, Vol.60, N. 8, P.1752-1761.
[9] Babichenko L.N., Tolmachev A.A., Chmilenko T.S., Sheikman A.K. Khimiya Geterotsikl. Soed., 1988, N.5, P.709-710.
[10] Tolmachev A.A., Babichenko L.N., Komarov I.V., Sereda S.V., Sheinkman A.K. Khimiya Geterotsikl. Soed., 1992, N.2, P. 183-189.
[11] Lanthanide Shift Reagents in Stereochemical Analysis, Ed: By Terence C. Morrill, VCH Publishers, 1986, P. 193.
[12] Tolmachev A.A., Dovgopoly S.I., Golod A.V., Babichenko L.I. Khimiya Geterotsikl. Soed.,1994, N 7, P.915-918.