Heteroatom Chemistry
Volume 14, Number 1, 2003

Reaction of ω-Carbonyl Substituted 1,3,3-Trimethyl-2-methyleneindolines with Phosphorus(III) Halides

Alexej A. Chekotylo, Alexandr N. Kostyuk, Alexandr M. Pinchuk, and Andrej A. Tolmachev

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Street 5, Kiev-94, 02094, Ukraine

Received 21 August 2001; revised 1 February 2002

ABSTRACT: *The phosphorylation of* N-*benzoyl-2-(1,3,3-trimethyl-2-methyleneindoline)acetamide (***2***) and ω-(3-dimethylamino)benzoyl-1,3,3-trimethyl-2-methyleneindoline (***6***) with phosphorus(III) halides resulted in the formation of 2,3-dihydro-4*H*-1,5,2-oxazaphosphinin-4-one and 1,2-dihydro-3*H*-phosphindol-3-one systems, respectively. The properties of the obtained compounds were studied. Further cyclization of 1,2-dihydro-3*H*-phosphindol-3-one into dihydrophosphindolo[3,2-c]pyrazole was carried out.*
 Heteroatom Chem 14: 23–28, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10060

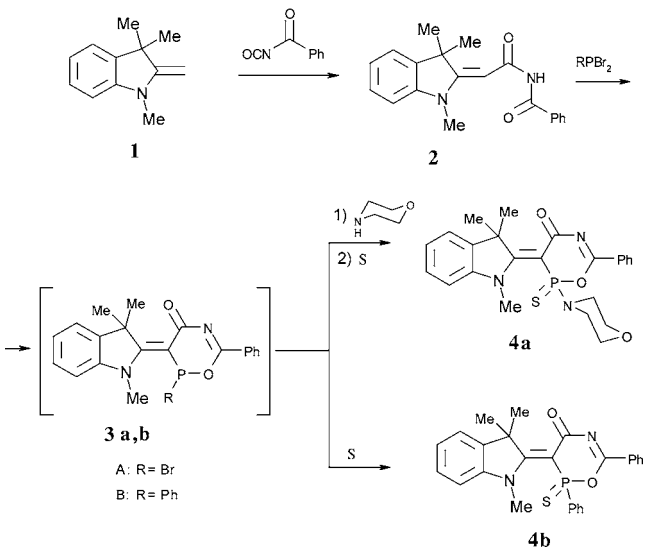
INTRODUCTION

During the past 10 years we have intensively studied the phosphorylation of enamines as well as electron-rich aromatic and heteroaromatic compounds with phosphorus(III) halides. With 1,3,3-trimethyl-2-methyleneindoline and its derivatives, this reaction was studied in detail [1,2]. These latter compounds bearing a C_β enamine nucleophilic carbon and in addition either N- or C-nucleophilic centres, were used for the syntheses of various phosphorus-containing heterocyclic compounds [3,4]. The carbonyl group at the exocyclic sp^2-hybridized carbon atom of 1,3,3-trimethyl-2-methyleneindoline significantly reduces the reactivity of the enamine moiety, e.g. ω-formyl-1,3,3-trimethyl-2-methyleneindoline does not react with phosphorus(III) halides. However, as shown in previous reports on phosphorylation of (3-dimethylamino)benzene carboxylic acid amides [5] and electron-rich diarylureas [6], formation of cyclic systems promotes C-phosporylation of aromatic substrates in spite of the deactivating influence of the substituent. In the present work, phosphorylation of ω-carbonyl derivatives of 1,3,3-trimethyl-2-methyleneindoline bearing both the enamine moiety and either O- or C-nucleophilic centers with phosphorus(III) halides was investigated in order to obtain new types of phosphorus-containing heterocyclic compounds.

RESULTS AND DISCUSSION

ω-Carbonyl derivatives of 1,3,3-trimethyl-2-methyleneindoline were obtained by addition of *N*,1-oxomethylenebenzamide to 1,3,3-trimethyl-2-methyleneindoline (**1**) or by its acylation with (3-dimethylamino)benzene carboxylic acid chloride (**5**) according to standard procedures [7]. Reactions of compound **2** with phosphorus tribromide and phenyldibromophosphine gave 1,5,2-oxazaphosphinines **3a** and **3b**, respectively (Scheme 1). Both compounds were not isolated, but their formation was confirmed by ^{31}P NMR data. Monitoring of the reaction of

Correspondence to: Alexej A. Chekotylo; e-mail: alexchek@mail.ru.



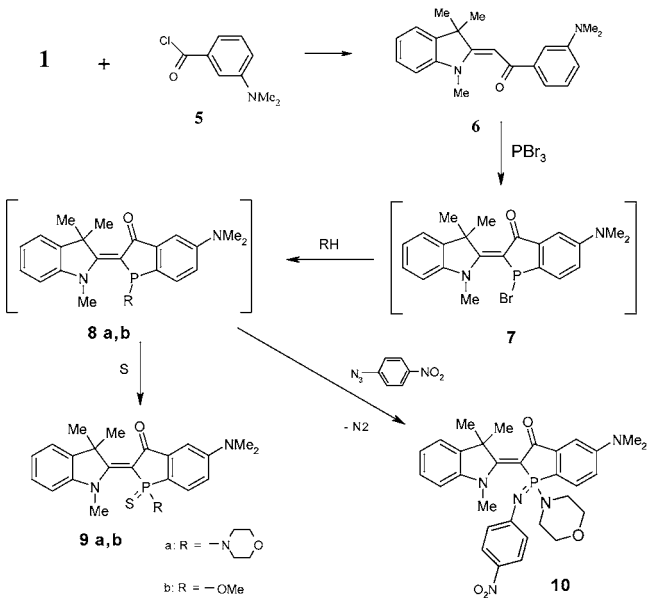
SCHEME 1

compound **2** with phenyldibromophosphine by ^{31}P NMR spectroscopy first revealed a signal at $\delta =$ 92 ppm, which then gradually transformed into a signal at $\delta = 36$ ppm, characteristic of compound **3b**. Compound **2** in reaction with phosphorus(III) halides theoretically can form two phosphorus-containing geterocyclic systems: four-membered and six-membered; however, as shown earlier, only one path way takes place in such cases, leading to formation of a six-membered oxazaphosphinic system [6,8]. This testifies that the first stage of the reaction probably takes place at the amide group. 1,5,2-Oxazaphosphinines **3a** and **3b** were converted into pentavalent phosphorus derivatives **4a** and **4b** and their structures were proved by ^{1}H NMR and IR spectroscopies. The ^{1}H NMR spectra of **4a** and **4b** do not reveal signals corresponding to N—H and C—H protons of the methylene group which were present in the starting compound **2a**, thus confirming the formation of cyclic products. In the IR spectrum, one absorption band characteristic of a carbonyl group in the region of 1705 cm^{-1} was observed and no absorption band corresponding to an N—H group could be found. It should be stated that, in the literature only one 1,5,2-oxazaphosphinine system fused onto aromatic and heteroaromatic rings was described [8,9].

ω-(3-Dimethylamino)benzoyl-1,3,3-trimethyl-2-methyleneindoline (**6**) bearing two C-nucleophilic sites—an enamine carbon atom and an electron rich carbon atom of a benzene ring—reacts with phosphorus tribromide to form 1-bromo-1,2-dihydro-3*H*-phosphindol-3-one (**7**) (Scheme 2). In the ^{31}P NMR spectrum of the reaction mixture two signals, corresponding to the starting and end products were observed, and no signals corresponding to the intermediate products could be found. This suggests that the first stage of the reaction is a limiting one and the subsequent intramolecular cyclization takes place rather quickly.

1-Bromophosphindolone (**7**) reacted with N- and O-nucleophiles to afford amide **8a** and ester **8b**, respectively, which could not be isolated individually and were transformed into the thioamide **9a** and the thioester **9b** by oxidation with elementary sulfur. Furthermore, the amide **8a** was transformed into the corresponding iminophosphonate **10** by the Staudinger reaction with *p*-nitrophenyl azide.

It is clear from the ^{1}H NMR spectra of compounds **9a,b** that closing of the phosphorus cycle in compound **7** goes only at the *p*-position to the dimethylamino group. The proton in the 7th position of the phosphindolone system gives a signal in the ^{1}H NMR spectrum in the region $\delta = 7.5$ ppm as a doublet of doublets. Also, the spin-coupling constant between the phosphorus atom and proton, $J_{PH} \sim 11$ Hz, is clear evidence of ortho-relationship of the phosphorus atom and proton. The latter is possible only in the case of the phosphorus ring closing in the *p*-position to the dimethylamino group. The second spin-coupling constant $J_{HH} \sim 8.5$ Hz is characteristic of aromatic protons, located in an ortho-relationship. The remaining two protons of the benzene ring are located in the *m*-position to



SCHEME 2

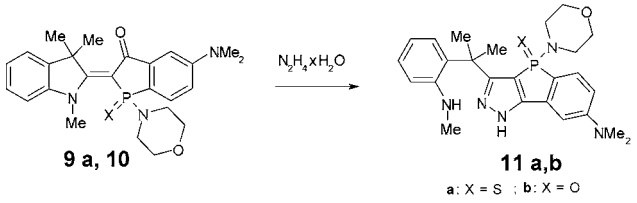
the phosphorus atom and have the spin-coupling constants $J_{PH} \sim 3$ Hz, whereas spin-coupling constants for protons, located in the *m*-position, are $J_{HH} \sim 2.5$ Hz.

Under similar conditions, the reaction of compound **6** with phenyldibromophosphine did not give the expected 1-phenylphosphindolone. Phosphindolones with an exocyclic C=C bond were previously not known, and the synthetic method described in the literature of 1,2-dihydro-3*H*-phosphindol-3-one by intramolecular cyclization of 2-carbethoxyphenylmethylphosphinic acid ester by the action of t-BuOK could provide only the pentavalent phosphorus derivatives [10].

It is known that ω-carbonyl derivatives of 1,3,3-trimethyl-2-methyleneindoline, in the course of reaction with hydrazine, undergo further cyclization into pyrazole derivatives [11]. It turned out that treatment of the thioamide **9a** with hydrazine effected the similar further cyclization into dihydrophosphindolo[3,2-*c*]pyrazole (**11a**). The reaction of the iminophosphinate **10** with hydrazine was accompanied by hydrolysis to yield the 4-oxodihydrophosphindolo[3,2-*c*]pyrazole (**11b**) (Scheme 3).

The structures of the products **11a,b** were confirmed by ^{1}H and ^{13}C NMR spectral data, as well as by IR spectroscopy. In the ^{1}H NMR spectrum of the compound **11a**, unlike that of **9a**, two signals corresponding to an N–H group are observed (exchange with D_2O): a singlet at $\delta = 10.1$ ppm and a quartet at $\delta = 3.8$ ppm ($^3J_{HH} = 4.5$ Hz). There is also a shift of the signal corresponding to the methyl group to the stronger field from $\delta = 3.7$ ppm (singlet) in **9a** to $\delta = 2.6$ ppm (doublet $^3J_{HH} = 4.5$ Hz) in **11a**. In the ^{13}C NMR spectrum of **11a**, compared with that of **9a**, a strong field shift of the signal corresponding to a quaternary carbon atom bearing two methyl groups from $\delta = 52$ ppm (**9a**) to $\delta = 37$ ppm (**11a**) was observed. Also, there was no signal in the region of $\delta = 180$ ppm characteristic of a carbonyl group. In the IR spectrum of **11a**, unlike that of **9a**, two absorption bands of N–H groups can be observed and there is also no absorption band of a carbonyl group in the region of 1640 cm^{-1}. For compound **11b** the ^{1}H NMR spectrum did not exhibit a doublet of doublets characteristic of a p-substituted benzene ring. Additionally, the IR spectrum, apart from the changes described above, shows an absorption at 1190 cm^{-1} which can be assigned to a P=O group.

It should be noted that the dihydrophosphindolono[3,2-*c*]pyrazole system was previously synthesized by a 1,3-dipolar cycloaddition of diphenylnitrilimine to phosphindole [12].



9 a, 10 **11 a,b**

a: X = S ; **b**: X = O

SCHEME 3

EXPERIMENTAL

All the manipulations with air-sensitive compounds were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were purified by conventional procedures. Melting points were determined with an electrothermal capillary melting point apparatus and are uncorrected. The ^{31}P, ^{1}H, ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer (121, 300, and 75 MHz, respectively). Chemical shifts are reported relative to internal tetramethylsilane (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). Yields, analytical and ^{31}P NMR spectral data of compounds **2, 4a,b, 6, 9a,b, 10, 11a,b** are listed in Table 1, whereas ^{1}H NMR and IR spectral data of these compounds are listed in Table 2, and their ^{13}C NMR spectral data in Table 3.

*N-Benzoyl-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)acetamide (**2**)*

To a solution of 1.8 ml (10 mmol) of **1** in 15 ml of benzene, 1.47 g (10 mmol) of *N*,1-oxomethylenebenzamide was added at 20°C with stirring. The reaction mixture was left to stand for 12 h at 20°C, and the precipitate that had formed was filtered off and recrystallized from benzene.

*2-(4-Morpholinyl)-6-phenyl-2-thioxo-3-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-2,3-dihydro-4H-1,5,2λ^5-oxazaphosphinin-4-one (**4a**)*

To a solution of 0.67 g (2.1 mmol) of **2** and 0.6 ml (4.2 mmol) of triethylamine in pyridine maintained under an inert atmosphere of argon, 0.2 ml (2.1 mmol) of phosphorus tribromide was added at 0°C. After 12 h, 0.3 ml (2.1 mmol) of triethylamine, 0.18 ml (2.1 mmol) of morpholine, and 0.83 g (2.5 mmol) of sulfur were added. The reaction mixture was left to stand for 12 h. Pyridine was removed in vacuo, and the residue was washed with water and recrystallized from a mixture of ethanol and water.

TABLE 1 Yields, Analytical Data, and ^{31}P NMR Data of the Products Obtained

Compound	mp (°C)	Yield (%)	^{31}P NMR (Solvent)	Formula	Found (Calculated) (%)	
					N	P
2	174–175 (C_6H_6)	87		$C_{20}H_{20}N_2O_2$	8.92 (8.74)	
4a	198–199 (EtOH/H_2O)	70	58.9 ($CDCl_3$)	$C_{24}H_{26}N_3O_3PS$	9.15 (8.99)	6.51 (6.63)
4b	180–181 (EtOH)	75	54.7 (DMSO)	$C_{26}H_{23}N_2O_2PS$	6.15 (6.11)	6.59 (6.76)
6	132–133 (C_6H_6)	62		$C_{21}H_{24}N_2O$	8.87 (8.74)	
9a	225–226 (EtOH)	53	61.0 ($CDCl_3$)	$C_{25}H_{30}N_3O_2PS$	9.04 (8.99)	6.48 (6.62)
9b	116–117 (EtOH/H_2O)	45	80.8 ($CDCl_3$)	$C_{22}H_{25}N_2O_2PS$	6.73 (6.79)	7.42 (7.51)
10	154–155 (EtOH/H_2O)	62	23.0 (EtOH)	$C_{31}H_{34}N_5O_4P$	12.32 (12.25)	5.56 (5.42)
11a	276–277 (CH_3CN)	70	50.8 ($CDCl_3$)	$C_{25}H_{32}N_5OPS$	14.50 (14.54)	6.35 (6.43)
11b	284–285 (EtOH)	68	26.2 (DMSO)	$C_{25}H_{32}N_5O_2P$	15.11 (15.04)	6.81 (6.65)

*2,6-Diphenyl-2-thioxo-3-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-2,3-hydro-4H-1,5, 2λ^5-oxazaphosphinin-4-one (***4b***)*

To a solution of 0.67 g (2.1 mmol) of **2** and 0.6 ml (4.2 mmol) of triethylamine in 10 ml of pyridine maintained under an inert atmosphere of argon, 0.3 ml (2.1 mmol) of dibromophenylphosphine was added at 0°C. After 12 h, 0.83 g (2.5 mmol) of sulfur was added. The reaction mixture was left to stand for 12 h. Pyridine was evaporated, and the residue was washed with water and recrystallized from a mixture of ethanol and water.

TABLE 2 ^{1}H NMR and IR Spectral Data

Compound	^{1}H NMR Spectral Characteristic (ppm), J (Hz)	IR (cm^{-1}) (KBr)
2	1.73 (6H, s, CH_3, CH_3); 3.31 (3H, s, N—CH_3); 6.66 (1H, s, C=C—H); 6.80 (1H, d, $^3J_{HH}$ = 7.8, 7-H); 7.03 (1H, t, $^3J_{HH}$ = 7.5, 6-H); 7.22 (2H, m, 4,5-H,); 7.55 (3H, m, 3′,4′,5′-H); 7.95 (2H, d, $^3J_{HH}$ = 7.2, 2′,6′-H); 8.91 (1H, s, N—H) ($CDCl_3$)	
4a	1.72 (3H, s, CH_3); 1.76 (3H, s, CH_3); 3.44 (4H, m, N—$(CH_2)_2$); 3.67 (4H, m, O—$(CH_2)_2$); 3.82 (3H, s, N—CH_3); 6.93 (1H, d, $^3J_{HH}$ = 7.7, 7-H); 7.17 (1H, t, $^3J_{HH}$ = 7.7, 6-H); 7.29 (2-H, m, 4,5-H); 7.45 (2H, m, 3′,5′-H); 7.56 (1H, t, $^3J_{HH}$ = 7.2, 4′-H); 7.91 (2H, d, $^3J_{HH}$ = 7.2, 2′,5′-H) ($CDCl_3$)	1705 (C=O)
4b	1.75 (6H, s, CH_3, CH_3); 3.46 (3H, s, N—CH_3); 7.15 (2H, m, Ar); 7.31 (1H, t, $^3J_{HH}$ = 7.5, 6-H); 7.45 (3H, m, Ar); 7.63 (6H, m, Ar); 8.07 (2H, d.d., $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 15.6, 2′,6′-H) (DMSO-D^6)	1710 (C=O)
6	1.84 (6H, s, CH_3, CH_3); 3.0 (6H, s, N—$(CH_3)_2$); 3.26 (3H, s, N—CH_3); 6.01 (1H, s, C=C—H); 6.80 (2H, m, Ar); 7.00 (1H, t, $^3J_{HH}$ = 7.5, 6-H); 7.30 (5H, m, Ar) ($CDCl_3$)	1640 (C=O)
9a	1.73 (3H, s, CH_3); 1.95 (3H, s, CH_3); 3.07 (8H, s, $N(CH_3)_2$, $N(CH_2)$); 3.22 (2H, m, $N(CH_2)$); 3.56 (4H, m, $O(CH_2)_2$); 3.75 (3H, s, N—CH_3); 6.9 (1H, m, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 2.2, $^4J_{HP}$ = 3.5, 6-H,); 7.1 (2H, m, Ar); 7.2–7.3 (3H, m, Ar); 7.5–7.6 (1H, d.d., $^3J_{HH}$ = 8.6, $^3J_{HP}$ = 10.8, 7-H) ($CDCl_3$)	1640 (C=O)
9b	1.68 (3H, s, CH_3); 2.00 (3H, s, CH_3); 3.08 (6H, s, $N(CH_3)_2$); 3.6 (3H, d, $^3J_{HP}$ = 13.5, O—CH_3); 3.78 (3H, s, N—CH_3); 6.9 (1H, m, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4, $^4J_{HP}$ = 3.3, 6-H,); 7.09 (1H, d, $^3J_{HH}$ = 8.1, 7′-H); 7.12 (1H, m, 4-H); 7.2–7.3 (3H, m, 4′,5′, 6′-H); 7.67 (1H, d.d., $^3J_{HH}$ = 8.7, $^3J_{HP}$ = 11.1, 7-H) ($CDCl_3$)	
10	1.43 (3H, s, CH_3); 1.78 (3H, s, CH_3); 3.06 (8H, m, $N(CH_3)_2$, N—CH_2); 3.20 (2H, m, N—CH_2); 3.52 (4H, m, O—$(CH_2)_2$); 3.61 (3H, s, N—CH_3); 6.42 (2H, d, $^3J_{HH}$ = 8.4, 2″,6″-H); 6.97 (1H, d, $^3J_{HH}$ = 6.9, 6-H); 7.13 (1H, s, 4-H); 7.24–7.46 (5H, m, 4′,5′,6′,7′,7-H); 7.77 (2H, d, $^3J_{HH}$ = 8.4, 3″,5″-H) (DMSO-D^6)	1650 (C=O) 1310 (P=N)
11a	1.76 (3H, s, CH_3); 1.89 (3H, s, CH_3); 2.65 (3H, d, $^3J_{HH}$ = 4.8, N′—CH_3); 3.03 (8H, m, $N(CH_3)_2$, N—CH_2); 3.23 (2H, m, N—CH_2); 3.60 (4H, m, O—$(CH_2)_2$); 3.82 (1H, k, $^3J_{HH}$ = 4.8, N′—H); 6.57 (1H, d, $^3J_{HH}$ = 8.1, 3′-H); 6.67 (2H, m, 5′,6-H); 7.01 (1H, s, 8-H); 7.20 (1H, t, $^3J_{HH}$ = 7.5, 4′-H); 7.36 (1H, d, $^3J_{HH}$ = 6.9, 6′-H); 7.48 (1H, d.d., $^3J_{HP}$ = 10.8, $^3J_{HH}$ = 8.4, 5-H); 10.10 (1H, s, N—H) ($CDCl_3$)	3460 (N—H) 3170 (N—H) 685 (P=S)
11b	1.66 (6H, s, CH_3, CH_3); 2.77 (3H, s, N′—CH_3); 2.97 (8H, m, $N(CH_3)_2$, N—CH_2); 3.35 (2H, m, N—CH_2); 3.72 (4H, m, O—$(CH_2)_2$); 4.10 (1H, s, N′—H); 6.46 (1H, d, $^3J_{HH}$ = 8.2, 3′-H); 6.63 (2H, m, 5′,6-H); 6.83 (1H, s, 8-H); 7.11 (1H, t, $^3J_{HH}$ = 7.3, 4′-H); 7.30 (2H, m, 5,6′-H); 12.8 (1H, s, N—H) (DMSO-D^6)	3490 (N—H) 3160 (N—H) 1190 (P=O)

TABLE 3 ^{13}C NMR Spectral Data

Compound	*^{13}C NMR Spectral Characteristic (ppm), J (Hz). Solvent $CDCl_3$*
4b	23.8 (s, CH_3); 24.2 (s, CH_3); 33.6 (s, N—CH_3); 50.7 (d, $^3J_{CP} = 9.9$, 3′-C); 95.7 (d, $^1J_{CP} = 99.7$, C=*C*—P); 109.4 (s, 7′-C); 122.1 (s, 5′-C); 124.5 (s, 4′-C); 127.8 (s, 6′-C); 128.1–133.7 (Ph, Ph′); 140 (s, 7a′-C); 142.7 (s, 3a′-C); 160.6 (d, $^2J_{CP} = 13.2$, 2′-C); 167.1 (s, C=O); 173.8 (s, C=N).
9a	24.0 (s, CH_3); 26.5 (s, CH_3); 37.8 (s, N—CH_3); 40.3 (s, $N(CH_3)_2$); 44.7 (s, $N(CH_2)_2$); 52.3 (d, $^3J_{CP} = 3.9$, 3′-C); 67.2 (d, $^3J_{CP} = 6.8$, $O(CH_2)_2$); 104.7 (d, $^3J_{CP} = 11.0$, 6-C); 110.5 (s, 7′-C); 116.5 (d, $^2J_{CP} = 14.1$, 7-C); 121.6 (s, 5′-C); 124.1 (d, $^1J_{CP} = 105$, 7a-C); 124.9 (s, 4′-C); 127.5 (d, $^3J_{CP} = 9.9$, 4-C); 127.8 (s, 6′-C); 141.7 (s, 7a′); 141.9 (d, $^2J_{CP} = 12.6$, 2′-C); 143.5 (s, 3a′-C); 153.1 (d, $^4J_{CP} = 2.3$, 5-C); 180.8 (d, $^2J_{CP} = 11.3$, C=O).
11a	26.2 (s, C—*C*H_3), 30.0 (s, NH—CH_3), 30.3 (s, C—*C*H_3); 37.4 (s, *C*$(CH_3)_2$); 39.5 (s, $N(CH_3)_2$); 43.4 (s, $N(CH_2)_2$); 66.5 (d, $^3J_{CP} = 7.2$, $O(CH_2)_2$); 102.8 (d, $^3J_{CP} = 10.3$, 6-C); 108.6 (d, $^1J_{CP} = 127$, 3a-C; 110.8 (s, 3′-C); 111.3 (d, $^2J_{CP} = 13.9$; 5-C), 115.2 (s, 5′-C); 124.3 (d, $^1J_{CP} = 117.8$, 4a-C); 125.2 (s, 4′-C); 127.5 (s, 6′-C); 128.4 (d, $^3J_{CP} = 10.9$, 8-C); 135.4 (s, 8a, 1′-C); 146.2 (s, 2′-C); 152.4 (s, 7-C); 153.0 (s, 8b-C); 157.8 (s, 3-C).

*1-[3-(Dimethylamino)phenyl]-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-1-ethanone (***6***)*

To a solution of 8.25 g (50 mmol) of (3-dimethylamino)benzene carboxylic acid and 6.7 ml (50 mmol) of triethylamine in 75 ml of toluene, a solution of 3.7 ml (50 mmol) of $SOCl_2$ in 50 ml of toluene was added at 0°C. The reaction mixture was stirred first at 0°C for 20 min, and then at 40°C for 1.5 h. The solvent was removed, and to the residue, a solution of 8 ml (45 mmol) of **1** and 6.7 ml (50 mmol) of triethylamine in 30 ml of toluene was added with stirring. The reaction mixture was left to stand for 24 h at 20°C. The precipitate that had formed was filtered off, washed with water, dried and recrystallized from toluene.

*Solution of 1-Bromo-5-(dimethylamino)-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-1,2-dihydro-3H-phosphindol-3-one (***7***)*

To a solution of 0.72 g (2.1 mmol) of ω-(3-dimethylamino)benzoyl-1,3,3-trimethyl-2-methyleneindoline (**6**) and 0.6 ml (4.2 mmol) of triethylamine in 10 ml of pyridine maintained under an inert atmosphere of argon, 0.2 ml (2.1 mmol) of phosphorus tribromide was added at 0°C. The reaction mixture was left to stand for 48 h at room temperature. In the ^{31}P NMR spectrum of the solution one signal at $\delta = 87$ ppm was observed. Thus the solution of **7** in pyridine was used without further purification.

*5-(Dimethylamino)-1-(4-morpholinyl)-1-thioxo-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-1,2-dihydro-3H-1λ^5-phosphindol-3-one (***9a***)*

To a solution of **7** in pyridine 0.3 ml (2.1 mmol) of triethylamine, 0.19 ml (2.1 mmol) of morpholine and 0.08 g (2.5 mmol) of sulfur were added at 20°C. After 12 h, 50 ml of toluene was added to the reaction mixture and the resulting precipitate was filtered off. The solvent was removed in vacuo, the residue dissolved in $CHCl_3$, and the mixture was purified by column chromatography (silica gel, eluant—$CHCl_3$). $CHCl_3$ was removed in vacuo and the residue was recrystallized from ethanol.

*5-(Dimethylamino)-1-methoxy-1-thioxo-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-1,2-dihydro-3H-1λ^5-phosphindol-3-one (***9b***)*

To a solution of **7** in pyridine, 0.3 ml (2.1 mmol) of triethylamine, 0.01 ml (2.4 mmol) of dry methanol, and 0.08 g (2.5 mmol) of sulfur were added at 20°C. After 12 h, 50 ml of toluene was added to the reaction mixture and the resulting precipitate was filtered off. The solvent was removed in vacuo, the residue dissolved in $CHCl_3$, and the mixture was purified by column chromatography (silica gel, eluant—$CHCl_3$). $CHCl_3$ was removed in vacuo and the residue was recrystallized from ethanol–water.

*5-(Dimethylamino)-1-(4-morpholinyl)-1-[(4-nitrophenyl)imino]-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)-1,2-dihydro-3H-1λ^5-phosphindol-3-one (***10***)*

To a solution of **7** in pyridine, 0.3 ml (2.1 mmol) of triethylamine and 0.19 ml (2.1 mmol) of morpholine was added at 20°C, and after 0.5 h, 0.35 g (2.1 mmol) of 4-nitrophenylazide was added. After 12 h, 50 ml of toluene was added and the resulting precipitate was filtered off. The solvent was evaporated and the residue was recrystallized from ethanol.

*7-(Dimethylamino)-3-{1-methyl-1-[2-(methylamino)phenyl]ethyl}-4-(4-morpholinyl)-1,4-dihydro-4λ^5-phosphindolo[3,2-c]pyrazole-4-thione (***11a***)*

A mixture of 1 g (2.1 mmol) of **9a**, 10 ml of ethanol, and 10 ml of 99% hydrazine-hydrate was boiled for

10 h, the course of the reaction being monitored by thin layer chromatography. After cooling of the reaction mixture, the precipitate was filtered off and recrystallized from acetonitrile.

*7-(Dimethylamino)-3-{1-methyl-1-[2-(methylamino)phenyl]ethyl}-4-(4-morpholinyl)-1,4-dihydro-4λ^5-phosphindolo[3,2-c]pyrazol-4-one (***11b***)*

A mixture of 1 g (1.8 mmol) of **10**, 10 ml of ethanol, and 10 ml of 99% hydrazine-hydrate was boiled for 20 h, the course of the reaction being monitored by thin layer chromatography. The reaction mixture was cooled, and the precipitate that had formed was filtered off and recrystallized from ethanol.

REFERENCES

[1] Tolmachev, A. A.; Kostyuk, A. N.; Kozlov, E. S.; Pinchuk, A. M. Zh Obshch Khim 1990, 60, 1752–1761 (Russian). CA 114, 42934k.
[2] Tolmachev, A. A.; Kostyuk, A. N.; Kozlov, E. S. Zh Obshch Khim 1991, 61, 1333–1341 (Russian). CA 116, 21152e.
[3] Tolmachev, A. A.; Dovgopoly, S. I.; Kostyuk, A. N.; Komarov, I. V.; Pinchuk, A. M. Phosphorous Sulfur Silicon Relat Elem 1997, 123, 125–140.
[4] Tolmachev, A. A.; Dovgopoly, S. I.; Kostyuk, A. N.; Kozlov, E. S.; Pushechnikov, A. O.; Holzer, W. Heteroat Chem 1999, 10, 391–398.
[5] Chekotylo, A. A.; Yurchenko, A. A.; Tolmachev, A. A. Khim Geterotsikl Soedin 2001, 4, 569 (Russian).
[6] Pushechnikov, A. O.; Krotko, D. G.; Volochnyuk, D. M.; Tolmachev, A. A. Khim Geterotsikl Soedin 2001, 5, 710 (Russian).
[7] Tarshits, D. L.; Przhiyalgovskaya, N. M.; Suvorov, N. N. Khim Geterotsikl Soedin 1988, 11, 1472–1475 (Russian).
[8] Pushechnikov, A. O.; Krotko, D. G.; Volochnyuk, D. M.; Tolmachev, A. A. Synlett 2001, 6, 860–862.
[9] Rozinov, V. G.; Dmitrichenko, M. Yu.; Kolbina, V. E.; Dolgushin, G. V. Zh Obshch Khim 1999, 69, 1430–1438 (Russian). Russ J Gen Chem 1999, 69, 1377–1385 (English).
[10] Balthazor, T. M. J Org Chem 1980, 45, 2519–2522.
[11] Tolmachev, A. A.; Babichenko, L. M.; Dovgopoly, S. I.; Golod, A. V. Khim Geterotsikl Soedin 1994, 7, 915–918 (Russian). CA 122, 187479r.
[12] Sedqui, A.; Vebrel, J.; Lande, B. Chem Lett 1984, 965–968.