with the organophosphorus molecule, $O^4-H[O^4]\ldots N^1$ with parameters: $N^1\ldots O^4$, 2.90(2) Å, $O^4-H[O^4]$, 1.25(1) Å, $H[O^4]\ldots N^1$, 1.67(1) Å, angle $O^4-H[O^4]\ldots N^1$, 168(1)°.

CONCLUSIONS

1. 6-Methyl-3-methoxy-2,4,4-triphenyl-3-phenylimino-2,3,4,5-tetrahydro-1,2,3-diazaphosphorine exists as the monomer in the crystalline state.

2. The crystal and molecule structure of the tetrahydrodiazaphosphorine and its solvate with CH_3OH added at the P=N bond was determined.

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^{1}H AND ^{31}P NMR STUDY OF THE STRUCTURE OF 2-R-4-METHYL-6,6-DIPHENYL-1-PHOSPHA-2,3-DIAZABICYCLO [3.1.0]HEX-3-ENE AND 2,3,4,5-TETRAHYDRO-1,2,3-DIAZAPHOSPHORINE DERIVATIVES

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We were the first to report cycloaddition at the dicoordinated phosphorus P=C bond in the case of the reaction of 2-phenyl- and 2-acetyl-5-methyl-1,2,3-diazaphospholes with diphenyldiazamethane [1-3].

Since the reaction pathway and properties of the products formed are influenced by the structure of the starting compounds, we also studied the reaction of N-benzoyl-substituted diazaphospholes with diphenyldiazamethane. The reaction proceeds in all cases at room temperature with the release of N_2 and formation of crystalline 2-R-4-methyl-6,6-diphenyl-1-phospha-2,3-diazabicyclo[3.1.0]hex-3-enes (IIa-c). (See scheme on next page.)

Upon heating with alcohols and upon the introduction of dry HCl through solutions of (II) in CH_2Cl_2, the phosphorane ring of (II) opens to form tetrahydro-1,2-diaza-3-phosphorine derivatives (III)-(V) [2]. These phosphorines add sulfur [2].

The structure of (II)-(VI) was shown by elemental analysis, IR, ^{1}H and ^{31}P NMR, and mass spectroscopy (Table 1). The chemical shifts for the phosphorus nuclei in the three-membered ring for (II) are: −80 (IIa), −93 (IIb), and −90 ppm (IIc). For (III)-(VI), $\delta^{31}P$ is in the range from 67-92 ppm. Similar δP chemical shifts are typical for these environments of the phosphorus atom [4].

The ^{1}H NMR spectra provide more information on the structures of (II)-(VI); some of these data are summarized for (III)-(VI) in Table 1.

Let us now examine the proof of the structure of bicyclic compounds (IIa-c). Their ^{1}H NMR spectra are extremely simple. For example, the single proton of the three-membered ring in (IIb) gives a doublet with chemical shift δH 3.78 ppm ($^2J_{PH}$ = 21 Hz), i.e., the signal is in the usual resonance region for cyclopropane protons [5]. In (IIa-c), the gem-diphenyl group and the N=C bond adjacent to the three-membered ring lead to a strong down-field shift for this proton signal, which is also related to the inductive and magnetic effect of

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TABLE 1. ^{1}H and ^{31}P NMR Spectra of (III)-(VI)

Compound	δ, ppm						J, Hz		
	^{31}P	CH$_3$	OCH$_3$	Ph	H$_a$	H$_e$	$^2J_{ae}$	$^3J_{PCCH_a}$	$^3J_{PCCH_e}$
(IVa)	+92	2,15	3,42	6,9–7,4	3,08	2,85	–18	~0,5	6,2
(Va)	+90	2,26	3,73 (OCH$_2$)	6,9–7,4	3,28	3,04	–18	~0,5	6,0
(IIIb) *	+67	2,06	–	7,0–7,3	3,24	3,08	–18	~1	5,0
(IIIa)	+74	2,12	–	6,9–7,4	3,36	3,18	–18	~0,5	6,0
(VI)	+72	1,88	3,45	6,9–7,6	3,45	3,09	–18	~4 †	21,0

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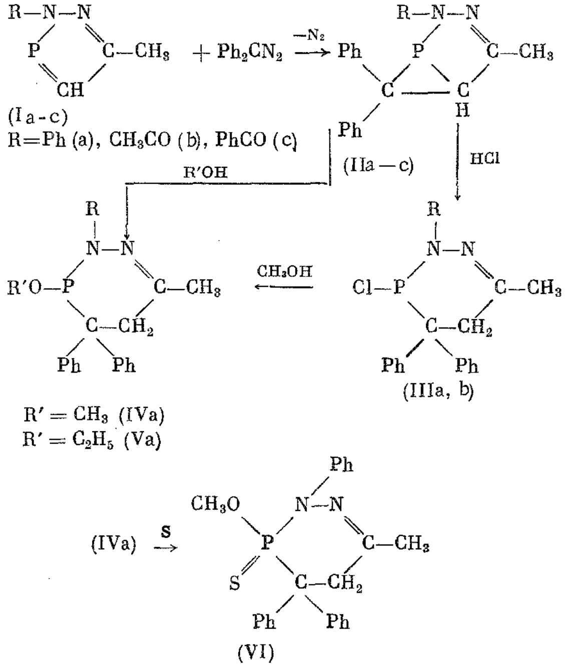
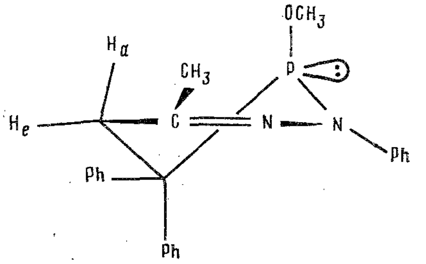
*The chemical shift of the C(O)CH$_3$ methyl group is 2.07 ppm.
†The the OCH$_3$ group doublet in CCl$_4$ solution overlaps the H$_a$ proton doublet. Thus, the subsequent ^{31}P splitting cannot be determined precisely.



the phosphorus atom. The protons of the methyl group at the unsaturated carbon atom resonate at δH 2.20 ppm. The corresponding chemical shifts for (IIa) and (IIb) are: δCH 3.88 (IIa) and 3.59 ppm (IIb), δCH$_3$ 2.12 ppm. The signal for the acetyl protons in (IIb) is found at δH 1.87 ppm (3H). The phenyl protons in IIa-c are found as broad bands at 6.5-7.1 ppm (10 H).

All compounds (III)-(VI) have generally similar ^{1}H NMR spectra. One such spectrum was given previously [2]. Table 1 shows that the H$_a$ and H$_e$ protons of the endocyclic methylene group are anisochronic and under conditions of total heteronuclear ^{1}H–{^{31}P} NMDR, these protons show a typical AB quadruplet as, for example, in the case of (IVa) with geminal coupling constant $^2J_{AB} = -18$ Hz. Subsequent spin–spin coupling of the lines of the AB quadruplet by the ^{31}P nucleus occurs with a small constant (~0.5 Hz) for the low-field doublet and with constant 6.2 Hz for the high-field doublet. This feature of the PMR spectrum indicates that, at room temperature, (IVa) exists predominantly in the half-chair conformation:



The methyl group at C(sp^2) is tentatively shown extruding from the plane of atoms $C^5-C^6=N-N$ and the downfield doublet may be assigned to the pseudoaxial H_a proton since the dihedral angle between the $C-H_a$ and C−P bonds is close to 90° and this angle is about 150° for the $C-H_e$ bond. An empirical dependence for $^3J_{P(III)OCH}$ on the dihedral angle between the planes in which the P−O and C−H bond lie and the angle characterizing the orientation of the unshared electron pair of the phosphorus atom relative to the O−C bond has been found for such angles. According to this dependence, the constants are 0 and ~8 Hz for the equatorial conformation of the orbital of the unshared electron pair of the trivalent phosphorus atom and 0 and ~15 Hz for the axial conformation of the unshared electron pair. Thus, the predominant conformation in (III)-(VI) is a half-chair with pseudoequatorial orientation of the phosphorus unshared electron pair. Such a conformation was found previously for (IVa) in the crystalline state by x-ray diffraction structural analysis [3].

In the case of the compound with the thiophosphoryl group (VI), the coupling of the phosphorus atom with the H_a proton has constant ~4 Hz, while this coupling with the H_e proton has constant $^3J_{P(III)CCH_e} = 21$ Hz. Comparison of these constants with the ^{1}H NMR spectral data for the stereoisomers of 2-methoxy-2-thio-4-methyl-1,3,2-dioxaphosphorinane [6] indicates that the half-chair conformation with pseudoaxial orientation of the thiophosphoryl group is predominant for (VI).

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Varian HA-100D spectrometer with TMS internal standard for 5 vol.% solutions in CCl_4. The ^{31}P chemical shifts were found by $^1H-\{^{31}P\}$NMDR and monitored by direct measurement on a YaMR-KGU-4 spectrometer.

2-Benzoyl-4-methyl-6,6-diphenyl-1-phospha-2,3-diazabicyclo[3.1.0]hex-3-ene (IIc). A solution of 0.8 g Ph_2CN_2 in CH_2Cl_2 was added to a solution of 0.8 g (Ic) [7] in CH_2Cl_2 in a drybox at about 20°C. The temperature of the reaction mixture was raised to 50°C. The vigorous release of N_2 ensued. The reaction was complete in 20 min. The reaction mixture was left to stand overnight and then filtered to yield 1.1 g (78%) crystalline (IIc) with mp 189-190°C (from ethanol). Molecular mass: found, 370; calculated, 370.4. IR spectrum (ν, cm^{-1}): 710, 725, 770, 790, 1500, 1600 (Ph), 1580 (C=N), 1640 (CO). Found: C, 74.48; H, 5.16; P, 8.51; N, 7.62%. Calculated for $C_{23}H_{19}N_2PO$; C, 74.57; H, 5.17; P, 8.36; N, 7.56%.

The syntheses of (IIa), (IIb), and (III)-(VI) were described in our earlier work [1, 2]. The authors thank Yu. Ya. Efremov and R. Z. Musin for taking the mass spectra.

CONCLUSIONS

1. The reaction of 2-R-5-methyl-1,2,3-diazaphospholes with diphenyldiazomethane leads to the formation of 2-R-4-methyl-6,6-diphenyl-1-phospha-2,3-diazabicyclo[3.1.0]hex-3-enes which, upon heating with alcohols and reaction with dry HCl, convert to derivatives of 2,3,4,5-tetrahydro-1,2-diaza-3-phosphorines.

2. The stereochemical dependence of the $^3J_{P(III)CCH}$ vicinal coupling constant on the dihedral angle for these phosphorines indicated predominant half-chair conformation with pseudoequatorial orientation of the phosphorus unshared electron pair orbital.

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