tion of the adamantyl and pyridyl rings, whereas such a process does occur in the case of the selenium analogs.

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REACTIONS OF DIAZAPHOSPHOLES WITH PHENYLDIAZOMETHANE

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UDC 542.91:547.1'118

Diphenyldiazomethane undergoes quantitative addition to the P=C bond of diazaphospholes with the formation of stable phosphirane-containing bicyclic compounds [1-3]. The reaction of 2-phenyl-5-methyl-1,2,3-diazaphosphole with diazomethane proceeds with the separation of nitrogen and the formation of a trimetric adduct of 1:1 composition [4].

In the present communication, the results of the investigation of the reaction of diazaphospholes with phenyldiazomethane are presented; analogies both with Ph_2CN_2 and with CH_2N_2 can be anticipated from this. According to the reactivity, 2-acetyl-5-methyl-1,2,3-diazaphosphole (AMDAP) proved to be far more active than the analogous 2-phenyl-substituted diazaphosphole (PMDAP). While $PhCHN_2$ reacts with the acetyldiazaphosphole at a temperature as low as −15°C, the reaction with the phenyldiazaphosphole proceeds sluggishly at 20°C. This is indicated by the intensive signal of $\delta^{31}P$ at 226 ppm for the initial diazaphosphole in the $\delta^{31}P$ NMR spectrum of the reaction mixture. The weak signals of $\delta^{31}P$ at 65 and −102.47 ppm can indicate the complex course of the reaction. The course of the reaction of AMDAP with $PhCHN_2$ is strongly influenced by the temperature, the order of the mixing, and the proportion of the reagents. A colorless precipitate is formed on the addition of AMDAP to a solution of $PhCHN_2$ in hexane with a 1:1 ratio of the reagents at −15°C. The precipitate is rapidly converted to a sticky mass from which a crystalline product with mp 160-161°C was obtained by treatment with ether and then recrystallization from CCl_4. According to the data of the mass spectrum and the elemental analysis, it is the 1:1 adduct of addition. The formation of the products of the two orientations (I) or (I') is possible in the reaction scheme.

The absence of the νNH band from the IR spectrum of the product and the appearance of a strong band at 3300 cm^{-1} in the spectrum of the crystals with mp 160-161°C can indicate that the Δ'-phosphapyrazoline derivative (I) or (I') formed in the first stage, isomerizes to the Δ^2-phosphapyrazoline derivative (II) or (II'). The PMR spectrum of the crystals with mp 160-161°C has the signals ($CDCl_3$, δ, ppm, J. Hz) $\delta H^1 = 5.05$, $^1J_{PH} = 42.7$; $\delta H^2 = 2.18$, $^4J_{N^1H^2} = 0.7$; $\delta H^3 = 2.32$, $^4J_{PH^3} = 0.9$. In the ^{31}P NMR spectrum, there is one signal, $\delta^{31}P = 30$ ppm (CH_2Cl_2). The PMR and ^{31}P NMR spectral data indicate that one isomer (II) or (II'), and not two as was the case for diazoacetic ester [5], is formed in the reaction of AMDAP with $PhCHN_2$. The choice in favor of the structure (II) was made by us on the basis of the analogy between the ^{13}C NMR spectra of AMDAP, PMDAP, the chloro- and methoxydiazaphospholines (IV) and (V), and the bicyclic compound (IV) were obtained for the correct assignment of the signals. The spectral parameters are presented in Table 1.

A. M. Butlerov Chemical Institute, Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 412-418, February, 1986. Original article submitted July 12, 1984.

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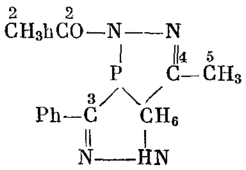
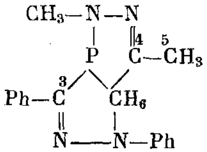
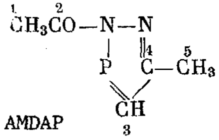
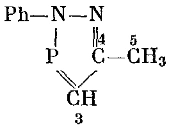
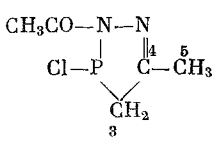
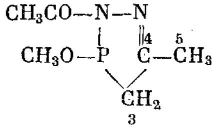
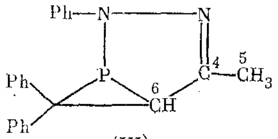
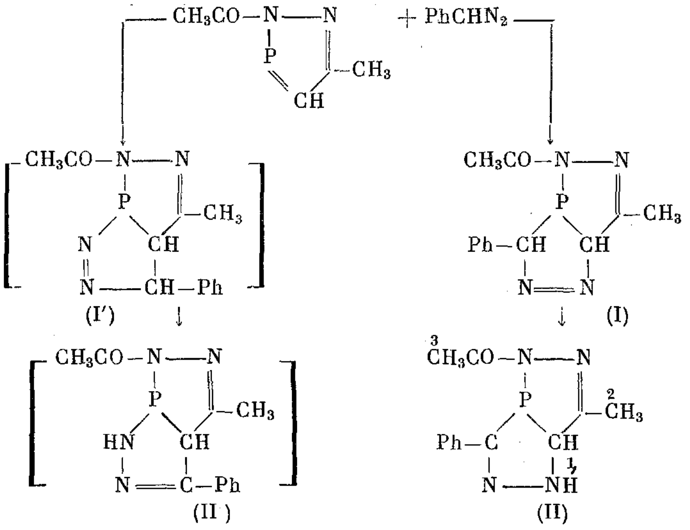
TABLE 1

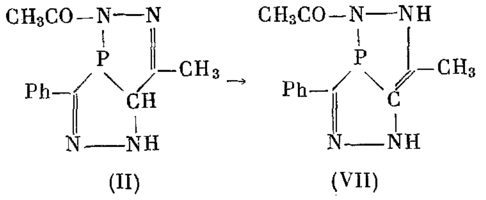
Compound	δ ^{13}C, ppm (J_{PC}, Hz)						
	C^1	C^2	C^3	C^4	C^5	C^6	Ph
 (II)	22,6 (0)			156,67 (2,21)	15,33 (0)	73,67 (14,71)	o=127,85 (5,148) m=126,67 (0) p=128,93 (0)
 (III)			151,1 (55,9)	148,0 (0)	16,3 (0)	75,6 (11,8)	i=135,0 (17,5) o=126,5 (5,2) m=129,2 (0) p=128,4 (0)
 AMDAP	22,16 (0)	172,61 (11,77)	144,44 (36,71)	158,77 (11,77)	15,73 (0)		
 PMDAP			137,26 (35,298)	156,10 (7,82)	15,73 (0)		i=144,08 (11,77) o=119,64 (8,82) m=128,94 (0) p=126,08 (0)

 (IV)	22,49 (0)	173,03 (10,29)	47,54 (27,94)	158,38 (0)	17,48 (0)		
 (V)	22,09 (0)	171,23 (10)	42,47 (19,12)	155,65 (5)	17,61 (0)	55,05 (7,35)	
 (VI)				151,69 (0)	18,85 (0)	53,94 (38,239)	

The close values of the signals of $\delta^{13}C^6$ – 73.67 and 75.6 ppm for (II) and (III), respectively – imply that their structures are identical. In the case of the inverse orientation (II'), the signal of $\delta^{13}C^6$ should be at higher field. For example, the bicyclic compound (VI), in which C^6 is linked to carbon and not to nitrogen, has $\delta^{13}C^6$ = 53.94 ppm.

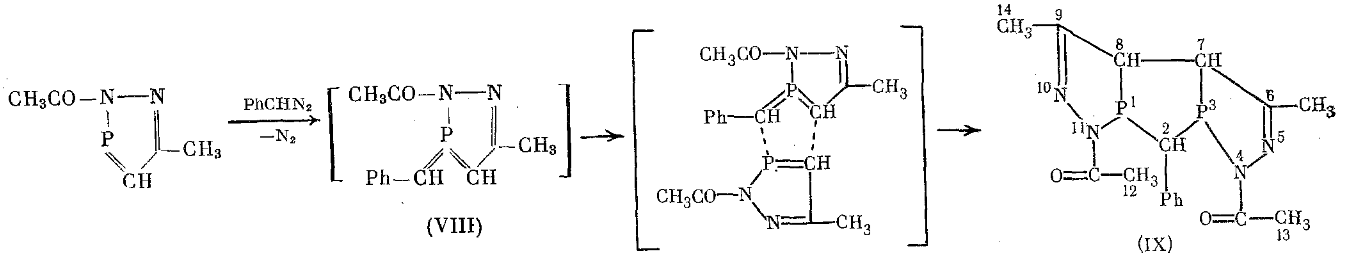


Therefore, the product of the reaction of AMDAP with $PhCHN_2$, which has the mp 160-161°C, is 2-acetyl-4-methyl-8-phenyl-1-phospha-2,3,7,8-tetraazabicyclo[3.3.0]octa-3,7-diene (II) and not its regioisomer (II'). The products of such an orientation are formed on the reaction of diazaphospholes with nitrilimines [6] and nitrile oxides [7]. A product with the indistinct mp 67-72°C was isolated after the separation of the Δ^2-phosphapyrazoline derivative (II) and the distillation of the residue in a high vacuum. Attempts to purify it by recrystallization, sublimation in a high vacuum, and by the method of column chromatography on silica gel were unsuccessful. The presence of two absorption bands of NH groups in its IR spectrum can indicate the isomerization of the isomer (II) to the product with two NH groups (VII).



A similar isomerization was previously observed in the reaction of diazaphospholes with diazoacetic ester [5].

The second route in the interaction of AMDAP with $PhCHN_2$ is the reaction with the separation of nitrogen. However, phosphirane-containing bicyclic compounds as observed in the case of Ph_2CH_2 [1-3] and $PhCh_3CN_2$ [8], are not formed. By performing the reaction at a higher temperature (0–10°C) and with the reverse order of the addition of the reagents to each other ($PhCHN_2$ was added to the diazaphosphole), the vigorous separation of nitrogen and the formation of the tricyclic compound (IX) were observed; (IX) is the product of the [2 + 3]-cycloaddition of the intermediate diylide (VIII) to the initial PMDAP.



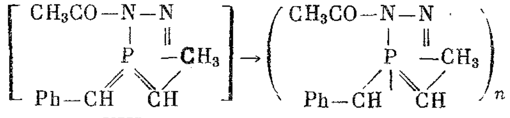
Compound (IX) – 4,11-diacetyl-6,9-dimethyl-2-phenyl-4,5,10,11-tetraaza-1,3-diphosphatricyclo-$[6.3.0.0^{3,7}]$undeca-5,9-diene – was isolated in an analytically pure form by the method of chromatography, and its structure was proved by the methods of IR, ^{31}P and ^1H NMR, and mass spectroscopy; $\delta^{31}P$ (CH_2Cl_2) = 90 ppm. The PMR spectral parameters are presented in Table 2.

TABLE 2. PMR Spectral Data of Compound (IX)

δ, ppm	J, Hz
$H^2=3,2$	$^2J_{H^2P^1}={}^2J_{H^2P^3}=28$
$H^{7,8}=4,00$	$^2J_{H^8P^1}={}^2J_{H^7P^3}=16,5$
	$^3J_{H^7P^1}={}^3J_{H^8P^3}=16,5$
$H^{12,13}=1,80;\ 2,27$	
$H^{14,15}=2,15$	

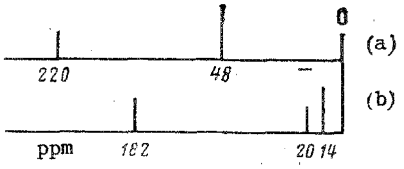
Two geometrical isomers of tricyclic compounds of the analogous structure were previously isolated in the reaction of AMDAP with 2-diazopropane; the analysis of their NMR spectra was performed [9, 10]. The comparison of the PMR spectra of the tricyclic compound (IX) with the spectra of the isomeric tricyclic compounds based on 2-diazopropane shows that the derivative (IX) has a symmetrical structure.

A substance with the indistinct mp 80-88°C was isolated besides the tricyclic compound (IX). The broad absorption bands in its IR and NMR spectra are characteristic of a polymer. The diylide (VIII), which is obtained in the first stage, evidently reacts with AMDAP at the moment of separation with the formation of the tricyclic compound (IX), and readily polymerizes at the P–C bond to the polymer (X).

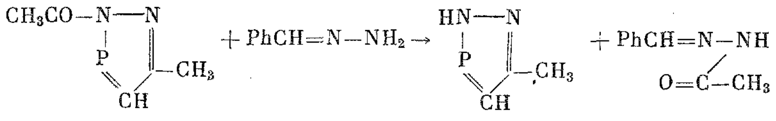


(VIII) (X)

The analogous conversion of diylide structures into trimers was observed in the reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole with diazofluorene [4]. The vigorous separation of nitrogen was observed on the addition of AMDAP to $PhCHN_2$ at 20°C. The ^{31}P NMR spectrum of the reaction mixture indicates the formation of very unstable products. The ^{31}P NMR spectra of the reaction mixture right after the reaction (a) and after 7 days (b) are presented below.



The signal with $\delta^{31}P$ = 48 ppm can appertain to the diylide; the signal at $\delta^{31}P$ = 220 ppm can appertain to 5-methyl-1,2,3-diazaphosphole (XI). AMDAP reacts with benzaldehyde hydrazone which could occur as an admixture in the solution of $PhCHN_2$. As a result, the diazaphosphole (XI) and benzylidene acetyl hydrazine are formed.



(XI)

The diazaphosphole (XI) was obtained [11] by the reaction of phenylhydrazine with 2-acetyl-5-methyl-1,2,3-diazaphosphole. However, the authors do not carry out the assignment of the signal of $\delta^{31}P$. We repeated this reaction and found that 5-methyl-1,2,3-diazaphosphole (XI) has $\delta^{31}P$ 220 ppm. Benzylidene acetyl hydrazine was isolated and characterized by the ^1H and ^{13}C NMR spectra and the IR spectrum. The diylide (VIII) is so reactive that it was only possible to identify it spectrally. The signal of $\delta^{31}P$ 48 ppm disappeared after 7 days; it was replaced by the new signals at 182, 20, and 14 ppm. The latter may pertain to the polymer. The signals at 182 and 20 ppm characterize the varied coordination of the phosphorus atom. The diylide evidently participates in the reaction with the diazaphosphole (XI) with the formation of a product containing two phosphorus atoms with different coordination. Its structure requires further investigations.

EXPERIMENTAL

IR spectra were taken on a UR-10 spectrometer using a suspension in mineral oil. PMR spectra were taken on Tesla BS-467A (60 MHz) and Bruker CXP-100 spectrometers. The ^{13}C NMR spectra were taken on a Bruker WH-90 spectrometer. The ^{31}P NMR spectra were taken on a KGU-4 spectrometer.

Reaction of AMDAP with $PhCHN_2$. a) Freshly distilled AMDAP was allowed to drop slowly with stirring in a current of nitrogen into a bright red solution of $PhCHN_2$ in hexane cooled to −15°C. The color of the reaction mixture changed to light yellow. A white residue appeared at the end of the addition of the reagent. The IR spectrum (ν, cm^{-1}) showed: 700, 1500, 1600 (Ph), 1525 (N=N), 1670 (C=O), etc. The residue obtained was transformed into a resinous mass from which the product (II) was isolated by treatment with ether and then recrystallization from CCl_4. It has mp 160-161°C; $\delta^{31}P = 30$ ppm (CH_2Cl_2). The IR spectrum of (II) (ν, cm^{-1}) showed: 700, 720, 770, 1500, 1600 (Ph), 1350, 1380, 1405, 1660 (CO), and 3300 broad (NH). The PMR spectrum ($CHCl_3$, δ, ppm): 5.05 doublet (CH, $^2J_{PH} = 42.7$ Hz), 2.18 doublet (CH_3–C=, $^4H_{H^1H^2} = 0.7$ Hz), and 2.32 doublet (CH_3CO, $^4J_{PH} = 0.9$ Hz). Found, %: C 54.91; H 4.74; N 22.96. The mol. wt. was 260 (from the mass spectrum). $C_{12}H_{13}OPN_4$. Calculated, %: C 55.43; H 5.04; N 22.55. The mol. wt. was 260.

The product (VII) was isolated after the separation of the product (II). Compound (VII) had mp 67-72°C. The IR spectrum (ν, cm^{-1}) showed: 700, 750, 775, 1490, 1600 (Ph), 1665 (CO), 3200, and 3400 broad (NH).

b) The bright red ether solution of $PhCHN_2$ was allowed to drop slowly into a solution of AMDAP in ether at −10°C in a current of nitrogen. The reaction mixture was warmed up, and its color turned to light yellow. After the addition of about a quarter of the portion of $PhCHN_2$, the light yellow sticky residue appeared on the sides of the flask. The residue was washed with hot CCl_4, and (IX) was obtained in the form of a white powder with mp 246-249°C. Analytically pure (IX) was obtained by the method of chromatography on silica gel, eluting with the 4:1 solvent mixture of benzene–ether; $\delta^{31}P = 90$ ppm (CH_2Cl_2). The IR spectrum (ν, cm^{-1}) showed: 700, 730, 795, 1500, 1600 (Ph), 1260, 1350, 1380, 1400, 1670, and 1690 (CO). Found, %: C 54.20; H 5.51; N 14.70; P 16.63. The mol. wt. was 374 (from the mass spectrum). $C_{17}H_{20}N_4P_2O_3$. Calculated, %: C 54.55; H 5.39; N 14.87; P 16.55. The mol. wt. was 374. Besides (IX), the hygroscopic powder of (X) with the indistinct mp of 80-88°C was isolated; it has $\delta^{31}P = 17$ ppm (CH_2Cl_2). The IR spectrum (ν, cm^{-1}) showed: 620, 860, 970 broad, 1050, 1115 broad, 1150 broad, and 1650.

c) To a solution of $PhCHN_2$ in ether was slowly added AMDAP at 20°C in a current of nitrogen. Nitrogen was liberated vigorously. The temperature of the reaction mixture increased sharply, and the color changed from red to yellow. Acetyl benzylidene hydrazine with the mp 131-132°C (CCl_4) was obtained. The IR spectrum (ν, cm^{-1}) showed: 690, 750, 1500, 1600 (Ph), 1670 strong shoulder (CO), and 3180 (NH). The PMR spectrum ($CDCl_3$, δ, ppm): 2.382 (CH_3), 7.250-7.836 (Ph), and 10.119 (NH). The ^{13}C NMR spectrum ($CHCl_3$, δ, ppm): 174.466 (CO), 144.115 (CH), 134, 107, 127, 185, 130.076, 128.745 (Ph), and 20.34 (CH_3). Found, %: C 67.07; H 6.30; N 17.39. $C_9H_{10}N_2O$. Calculated, %: C 66.60; H 6.17; N 17.28.

CONCLUSIONS

The action of 2-acetyl-5-methyl-1,2,3-diazaphosphole on phenyldiazomethane at −15°C in hexane leads to 2-acetyl-4-methyl-8-phenyl-1-phospha-2,3,7,8-tetraazabicyclo[3.3.0]octa-3,7-diene. The inverse action of phenyldiazomethane on 2-acetyl-5-methyl-1,2,3-diazaphosphole at 0°C in ether gives 4,11-diacetyl-6,7-dimethyl-2-phenyl-4,5,10,11-tetraaza-1,3-diphosphatricyclo[$6.3.0.0^{3,7}$]undeca-5,9-diene.

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SYNTHESIS AND EQUILIBRIUM OF STEREOISOMERS OF 5-PHENYL-2-ETHOXY-1,3,5-DIOXAPHOSPHORINANE

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and A. S. Ionkin

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On the vacuum distillation of tris(hydroxymethyl)phenylphosphonium chloride with subsequent neutralization by alkali, 5-phenyl-1,3,5-dioxaphosphorinane was obtained [1]. Comparison of the PMR spectra of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane [2] (the model of the form A with the axial orientation of Ph on P) and 1,3-di-p-tolyl-5-phenyl-1,3,5-diazaphosphorinane [3] (the model of the form B with the equatorial orientation of Ph on P) showed that the conformational equilibrium is displaced in favor of the form A. This was confirmed by the comparison of the experimental and calculated dipole moments of the compounds. The form B predominates in the equilibrium of the conformers of 1-phenylphosphorinane [4] at −80°C and of the stereoisomers of 1-phenyl-4-tert.butylphosphorinane [5] at 140°C. The corresponding proportions are 65 and 55%; this also testifies to the absence of significant temperature dependence. Analogous results were obtained in the study of 1-phenylphosphorinan-4-ones [6, 7].

The shift of the equilibrium in favor of the form A in passing from the phosphorinanes to the 1,3,5-dioxaphosphorinanes was explained by the donor properties of the phenylphosphino group; these properties appeared with the equatorial orientation of the unshared electron pair of the P atom [8]. The shift of the equilibrium in favor of the form A in 2,5-diphenyl-1,3-2,5-dioxaboraphosphorinane [2] is a confirmation of this hypothesis, since the B—Ph possesses acceptor properties and assists the manifestation of the donor properties of the phenylphosphino group. For the further confirmation of the hypothesis, it was of interest to introduce a donor group at the two position of 5-phenyl-1,3,5-dioxaphosphorinane which should prevent the manifestation of the donor properties of the phenylphosphino group and displace the equilibrium in favor of the form B.

Attempts were made in [1] to obtain 5-phenyl-1,3,5-dioxaphosphorinanes by the reaction of bis(hydroxymethyl)phosphine with aldehydes. However, heating with paraformaldehyde at 180°C or in benzene with the azeotropic distillation of water in the presence of p-toluenesulfonic acid of BF_3 etherate did not lead to a reaction. The use of CH_3CHO, i-PrCHO, and PhCHO instead of paraformaldehyde likewise did not lead to a reaction. Acetals of aldehydes and orthoformic ester were utilized in the present work. The ethoxy group has a combination of electronic effects which relate it to donors [9].

Bis(hydroxymethyl)phenylphosphine has two nucleophilic centers: the P and O atoms. Two types of substitution products may correspond to this. The reaction with $CH_3CH(OEt)_2$ and $PhCH(OEt)_2$ proceeded at the boiling or without heating with BF_3 etherate and gave the products of substitution at the P atom. The signals of bis(α-ethoxyethyl)- and bis(ethoxybenzyl)phenylphosphines (−12 and −8.18 ppm) were present in the ^{31}P NMR spectra of the reaction mixtures; this was based on the comparison with the spectra of bis(α-hydroxyethyl)- and bis(hydroxybenzyl)phenylphosphines [10, 11]. Reaction with orthoformic ester gave the product of substitution at the O atom. The structure of the compound obtained was established by the methods of IR spectroscopy, ^1H and ^{31}P NMR spectroscopy, and mass spectrometry.

The absorption of the hydroxyl groups is absent from the IR spectrum. Signals of the methyl, hydroxymethylene, methine, phosphinomethylene, and phenyl protons, with the 3:2:1:4:5 ratio of intensities, are present in the PMR spectrum. The values of the chemical shifts

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