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STRUCTURE OF 4,4'-DIDEHYDROBIS(5-METHYL-2-PHENYL-1,2,3-DIAZAPHOSPHOLA) AND 4,4'-DIDEHYDROBIS(2-PHENYL-5-R-1,2,3-DIAZAARSOLES)

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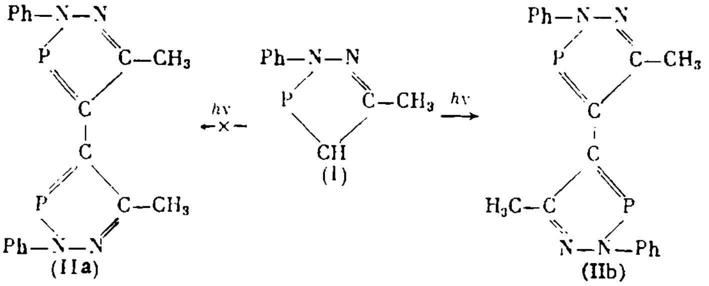
UDC 542.91:548.737:541.14:547.1'118:547.794

We have previously shown [1-3] that UV irradiation of 5-methyl-2-phenyl-1,2,3-diazaphosphole (I) affords a crystalline product, which according to its PMR, ^{31}P NMR, and mass spectra was assigned the structure (IIa) or (IIb) [3].



A final choice between (IIa) and (IIb) was made from an x-ray diffraction study, in favor of (IIb), 4,4'-didehydrobis-(5-methyl-2-phenyl-1,2,3-diazaphosphole), which contains the 1,4-diphosphabuta-1,3-diene fragment with the S-trans configuration, and two-coordinated phosphorus atoms.

UV irradiation of 2,5-diphenyl-1,2,3-diazaarsole (III) and 5-methyl-2-phenyl-1,2,3-diazaarsole under similar conditions did not give the corresponding 4,4'-didehydrobis(diazaarsoles).

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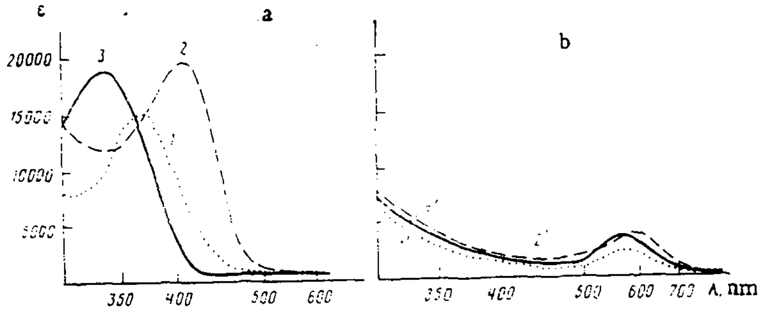
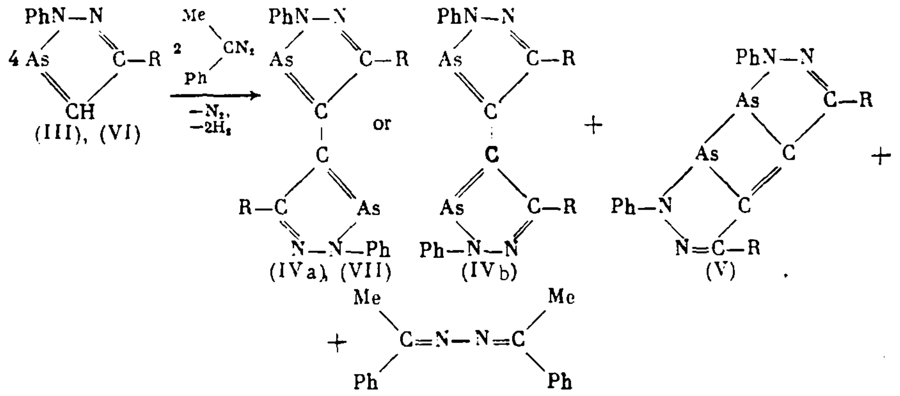


Fig. 1. UV spectra of freshly-prepared (a) and color-changed solutions (b) in CCl_4 of (VII) (1, 1'), (IVa) (2, 2'), and (IIb) (3, 3').

Reaction of (III) with methylphenyldiazomethane in a mixture of ether and pentane at -20°C afforded yellow crystals, mp 217-218°C, and claret-colored crystals mp 250-250.5°C, corresponding (from their mass spectra) to two molecules of the diazaarsole (III) less two hydrogen atoms [3]. In the absence of a solvent, or on heating in ether, only the product mp 250-250.5°C and acetophenone azine were formed.

According to its UV (Fig. 1) and IR spectra (see Experimental), the compound with mp 250-250.5°C obtained from (III) may be assigned the structure (IVa) or (IVb). Unfortunately, the quality of the crystals of (IV) did not permit an x-ray study to be carried out. This could, however, be done with the methyl derivative (R = Me), and this was found to be the S-trans isomer (VII).



R = Ph(III), (IV), (V), Me(VI), (VII).

The structure of (IVa) was confirmed indirectly by the similar behavior of CCl_4 solutions of (IVa) and (IIb) in light. In both instances, the color of the solution and the UV spectrum underwent changes. In the UV spectrum of (IVa) (in CCl_4), the absorption with λ_{max} 410 nm (ε 19,253.6) disappeared, while a peak with λ_{max} 596 nm (ε 4480.7) appeared (Fig. 1), the solution becoming blue in color. The isolated blue product had mp 208-210°C, and the same molecular mass as (IVa).

The similarity of the structures of (IVa) and (IIb) was also apparent from the fact that in both cases UV irradiation of the CCl_4 solutions at liquid nitrogen temperatures gave radicals which could be identified by EPR. The radical center was located on carbon, rather than on arsenic (or phosphorus).

The other product of the reaction of (III) with methylphenyldiazomethane, melting at 217-218°C, showed different UV and IR spectra, differing slightly from (IVa), and its CCl_4 solution did not change color in light. On recrystallization from acetonitrile, it underwent change (see Experimental), but its molecular mass remained unchanged (M 562). These differences point to the structure (V). It was unfortunately not possible to carry out an x-ray structural examination of these crystals as a result of their poor quality. It is interesting that previous attempts by the authors [4] to synthesize 1,4-diphosphabuta-1,3-dienes gave the [2 + 2]-cycloaddition products. It is thus possible that (V) is formed from S-cis-1,4-diphosphabuta-1,3-diene (IVb).

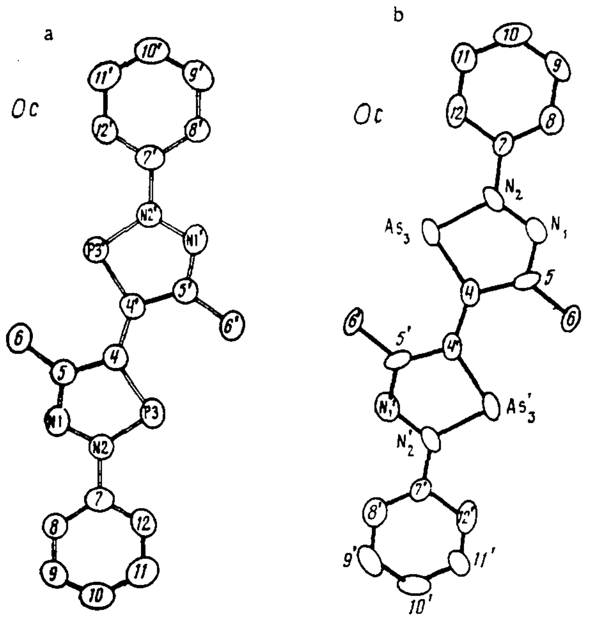
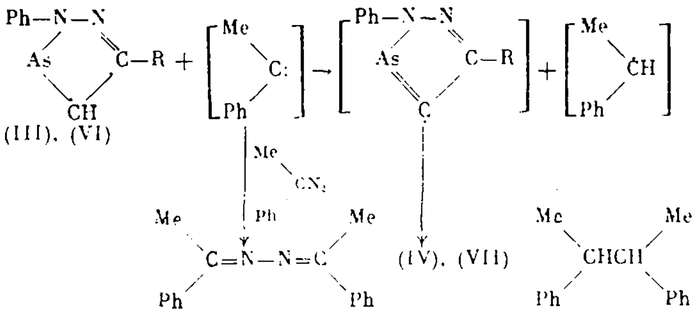


Fig. 2. Molecular geometry of (IIb) (a) and (IVa) (b).

The reaction of 5-methyl-2-phenyl-1,2,3-diazaarsole (VI) with methylphenyldiazomethane affords acetophenone azine and a yellow, crystalline product with mp 179-180°C, which from its mass spectrum is a dimer of (VI) without two of its hydrogen atoms. The PMR spectrum (in CCl_4, δ, ppm) showed signals for the Me groups at 2.57 (s) and the benzene ring at 7.17 (m), no signal being seen for hydrogen at the As=C bond. The IR spectrum is reminiscent of that of (IVa). Like (IVa), its solution in CCl_4 turned blue in light, the absorption with λ_{max} 373 nm (ε 13,506.3) disappearing and weak absorption at 589 nm (ε 2569.3) appearing (Fig. 1). These findings suggest that the compound mp 179-180°C is the S-trans-isomer of 4,4'-didehydrobis-(5-methyl-2-phenyl-1,2,3-diazaarsole), and this has been confirmed by x-ray structural analysis (see below).

The mode of formation of 4,4'-didehydrobis-(diazaarsoles) on reaction of diazaarsoles (III) and (VI) with methylphenyldiazomethane is far from clear. The reaction probably proceeds via the formation of methylphenylcarbene, which removes a hydrogen radical from the As=CH group, the resulting radicals undergoing coupling. Reaction of the carbene with the diazo compound gives acetophenone azine. The formation of the carbene under the reaction conditions is evidently initiated by the original diazaarsole:



Reaction of (VI) with methylphenyldiazomethane at 85°C in the presence of $CuSO_4$ afforded the same products, the yield of (VII) being 9%, and of acetophenone azine, 17%.

When (VI) was reacted with methylphenyldiazomethane, in addition to the products mentioned there was obtained a low-melting, crystalline compound which decomposed in air with vigorous evolution of gas, followed by polymerization. This crystalline product may be the unstable [2 + 3]-cycloadduct.

An x-ray structural analysis of 5-methyl-2-cyanoethyl-1,2,3-diazaphosphole has been reported [5], together with 2,5-dimethyl-1,2,3-diazaphosphole hydrochloride [6] and 1,5-dimethyl-

1,2,3-diazaphosphole [7]. Some structures have been examined by electron diffraction in the gas phase [8, 9].

Compounds of two-coordinated arsenic atoms have received much less attention. Arsabenzenes are known [5], and we have previously [10] examined the structure of 2,5-diphenyl-4-diphenylmethyl-1,2,3-diazaarsole.

The heterocycles in all the molecules examined are planar. In (IIb), the heterocycle $N^1N^2P^3C^4C^5$ (1) is planar to within 0.009(3) Å, and in (VII) the heterocycle $N^1N^2As^3C^4C^5$ (2) to within 0.007(10) Å. The dihedral angles between the planes of the phenyl substituents and the planes (1) and (2) are 14.6 and 16.3°, respectively.

The molecules of (IIb) and (IVa) are planar, resulting in short intramolecular contacts $P^3 \ldots C^6$ (3.108 Å) and $As^3 \ldots C^6$ (3.074 Å), which are probably responsible for the increased external valence angles at C^4 and the angles $C^4C^5C^6$, both in (IIb) and (VII). Despite this, the molecules are stable, as a result of conjugation between the diazaphosphole and the diazaarsole rings. Conjugation is more clearly apparent in the phosphorus compound (IIb), the bonds therein being more delocalized than in the arsenic compound (VII).

Comparing the x-ray structural data for (IIb) and (VII) with the available data for diazaphospholes [5, 6] and diazaarsole [10], it is noteworthy that the $E^3{=}C^4{-}C^4{=}E^3$ fragment (E = P, As) in (IIb) and (VII) is more highly conjugated.

The bond lengths and valence angles in the phenyl substituents in (IIb) and (VII) have the usual values.

EXPERIMENTAL

IR spectra were recorded on a Specord 751R instrument, and PMR spectra on a Tesla BS-467 NMR spectrometer (operating frequency 60 MHz), internal standard hexamethyldisiloxane. Mass spectra were obtained on a Finigan MAT-212 instrument at 50-120°C. UV irradiation was carried out with a PTK-5 mercury-quartz lamp through Pyrex glass. EPR spectra were obtained on an RE 1306 instrument, with irradiation by a DRShA-250 lamp. UV spectra were recorded on a Specord UV-VIS instrument.

Reaction of 2,5-Diphenyl-1,2,3-diazaarsole (III) with Methylphenyldiazomethane. c) In ether/pentane. To a solution of 1.9 g of the diazo compound in 30 ml of pentane was added dropwise a solution of 4 g of the diazaarsole (III) (mp 61-62°C) in 20 ml of diethyl ether. There was a slight evolution of gas. On the following day, small yellow crystals had separated on the walls of the flask (V). After three days, claret-colored crystals had separated (IVa). The mixture was left to stand for 15 days. The crystals of (V) and (IVa) were filtered off and washed with ether, overall yield 0.6 g (15%). Products (V) and (IVa) were separated by mechanical sorting. Compound (V): mp 217-218°C. Found: M 562 (mass spectrum). $C_2H_{20}As_2N_4$. Calculated: M 562. IR spectrum (vaseline oil, ν, cm⁻¹): 670, 680, 725, 730 s (Ph), 1037 med, 1250 s, 1470 v.s, 1575 s (Ph). Compound (IVa): mp 250-250.5°C. Found: M 562 (mass spectrum). $C_{28}H_{20}As_2N_4$. Calculated: M 562. IR spectrum (vaseline oil, ν, cm⁻¹): 670, 680, 730, 740 s (Ph), 1268 v.s, 1480 v.s, 1580 s (Ph). On recrystallization from acetonitrile, (V) isomerized to a yellow crystalline solid, mp 232-233°C. Found: N 10.28%, M 562 (mass spectrum). $C_{28}H_{20}As_2N_4$. Calculated: N 9.96%, M 562. IR spectrum (vaseline oil, ν, cm⁻¹): 565, 580 med, 670, 680 med, 735 s (Ph), 765 w, 972 s, 1012 v.s, 1260 s, 1480, 1580 med (Ph), 1790 v.s, etc. A solution of (IVa) in CCl_4 isomerized in light to a blue crystalline solid, mp 208-210°C. Found: M 562 (mass spectrum). $C_{28}H_{20}As_2N_4$. Calculated: M 562. IR spectrum (vaseline oil, ν, cm⁻¹): 675, 685 med, 738 s (Ph), 1270 v.s, br., 1440 v.s, 1465 v.s, 1576 s (Ph), 1720 s. Following removal of (V) and (IVa), the filtrate deposited lustrous yellow crystals of acetophenone azine. These were twice filtered off and washed with ether. Yield 0.3 g (54%), mp 122.5-123°C (from hexane). IR spectrum (vaseline oil, ν, cm⁻¹): 550 med, 674 s, 740 s (Ph), 1005 med, 1270 s, 1340 s, 1426 v.s, 1475 med, 1588 s (Ph), 1548 med (C=N), etc. PMR spectrum (CCl_4, δ, ppm): 2.3 s (CH_3), 7.2 m (Ph). Found: C 80.61; H 7.02; N 12.02%. $C_{16}H_{16}N_2$. Calculated: C 81.36; H 6.78; N 11.86%.

Reaction of 2,5-Diphenyl-1,2,3-diazaarsole with Cyclohexanone. To a solution of 2 g of the diazaarsole (III) in 5 ml of dichloromethane was added carefully 0.7 g of cyclohexanone. After 12 days, crystalline (IVa) began to separate from the mixture, which slowly became viscous. After 29 days, the (IVa) was filtered off and washed with dichloromethane (0.2 g). After 24 days,* repeated precipitation of the filtrate with ether and filtration gave a further 0.5 g of (IVa) (0.7 g in all). The overall yield was 35%. This material (IVa) was contaminat-

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*As in Russian original — Publisher.

TABLE 1. Coordinates of Nonhydrogen Atoms

Atom	(IIb)			(VII)		
	X	*Y*	*Z*	*X*	*Y*	*Z*
E (P, As)	0.3899(1)	0,0192(4)	0.2096(1)	0,4105(3)	0,00693(5)	0.2243(2)
N^1	0.2301(4)	1.1272(1)	0.1347(3)	0.233(2)	0.1239(4)	0.146(1)
N^2	0.4291(4)	0.0907(1)	0.2350(3)	0.439(2)	0.0903(4)	0.251(1)
C^4	0.0896(5)	0.0242(1)	0.0503(3)	0.092(4)	0.0230(5)	0.056(1)
C^5	0.0422(5)	0,0905(2)	0,0335(3)	0.049(2)	0.0889(6)	0.044(1)
C^6	−0.1969(5)	0,1235(2)	−0,0829(4)	−0.193(2)	0.1204(6)	−0.074(2)
C^7	0.6535(5)	0.1220(1)	0.3536(3)	0.643(2)	0.1246(5)	0.368(2)
C^8	0.6390(5)	0.1847(2)	0.3923(4)	0.623(3)	0.1851(6)	0.410(2)
C^9	0,8574(6)	0,2150(2)	0.5036(4)	0.835(3)	0,2181(6)	0.521(2)
C^{10}	1,0890(6)	0,1820(2)	0,5773(4)	1,077(3)	0.1875(7)	0.590(2)
C^{11}	1.1018(5)	0.1194(2)	0,5410(4)	1.101(3)	0.1276(6)	0,556(2)
C^{12}	0.8857(5)	0.0895(1)	0,4282(4)	0,895(3)	0,0940(6)	0.446(2)

ed with the oxide As_4O_6, M 396 (mass spectrum). It was removed by sublimation *in vacuo* (4 mm, at 150-200°C), and also by dissolving the product (V) in benzene.

Reaction of 5-Methyl-2-phenyl-1,2,3-diazaarsole (VI) [11] with Methylphenyldiazomethane. To a solution of 1.8 g of methylphenyldiazomethane in 25 ml of light petroleum (bp 40-60°C) was added carefully 3 g of the diazaarsole (VI) (bp 84°C, $5.6 \cdot 10^{-2}$ mm). There was a slow evolution of gas (N_2 and H_2). After one day, the mixture was filtered, and the mixture of yellow, lustrous crystals of 4,4'-didehydrobis-(5-methyl-2-phenyl-1,2,3-diazaarsole) and As_4O_6 washed with ether. The product (VII) was recrystallized from ethanol, mp 179-180°C. IR spectrum (vaseline oil, ν, cm^{-1}): 510 w, 635 med, 678 s, 740 v.s (Ph), 892 s, 1063 w, 1262 v.s (planar vibrations of the diazaarsole ring), 1318 med, 1480 v.s, 1578 s (Ph). Found: C 49.08; H 3.65; N 12.54%. M 438 (mass spectrum). $C_{18}H_{16}As_2N_4$. Calculated: C 49.32; H 3.65; N 12.79%. M 438.

X-Ray Diffraction Examination. The crystals of (IIb), $C_{18}H_{16}N_4P_2$, mp 150°C, were monoclinic, with (at 20°C) $a = 5.254(1)$, $b = 21.177(5)$, $c = 7.972(2)$ Å, $\beta = 107.29(2)°$, $d_{calc} = 1.37$ g/cm³, $Z = 2$, space group $P2_1/n$, the molecule in a special position in the center of symmetry. The crystals of (VII), $C_{18}H_{16}As_2N_4$, mp 179°C, were isostructural with those of (IIb). At 20°C, $a = 5.265(3)$, $b = 21.566(9)$, $c = 7.950(7)$ Å, $\beta = 107.48(4)°$, $d_{calc} = 1.69$ g/cm³. The crystals of (VII) were systematically twinned, the cell parameters being found by excluding in the INDEX procedure those reflections which were connected by short vectors. The cell parameters and the intensities of 841 (IIb) and 632 (VII) reflections with $F^2 \geq 5\sigma$ were measured on an Enraf–Nonius CAD-4 automatic K-diffractometer (λMoK_α, graphite monochromator, $\omega/5/3\theta$ (IIb) and $\theta/2\theta$ (VII) scanning, $\theta \leq 25°$). The structure of (IIb) was calculated directly using the MULTAN program, and refined in anisotropic approximation. All the hydrogen atoms were located from the difference series, and refined isotropically. The final values of the divergence factors were $R = 0.035$ and $R_w = 0.046$. The coordinates of the nonhydrogen atoms in (VII) were given by the equal coordinates of the corresponding atoms in (IIb), and refined in anisotropic approximation. The hydrogens of the phenyl substituent were located in the calculated positions, and those of the methyl group from the difference series. The contributions of the hydrogen atoms to the structural amplitudes were taken into account in the final stage of refinement with fixed positional and isotropic temperature parameters ($B_{iso} = 5$ Å). All calculations were carried out on a PDP 11/23 computer using the SDP program. The parameters of the nonhydrogen atoms in (IIb) and (VII) are given in Table 1, and the bond lengths and valence angles may be obtained from the authors. The molecular geometry of (IIb) and (IVa) is shown in Fig. 2.

The authors thank V. I. Morozov for obtaining the EPR spectra and for useful discussions.

CONCLUSIONS

1. The 1,4-diphosphabuta-1,3-dienes S-trans-4,4'-didehydrobis-(5-methyl-2-phenyl-1,2,3-diazaphosphole (and diazaarsole), and S-trans-4,4'-didehydrobis-(2,5-diphenyl-1,2,3-diazaarsole) have been obtained. The structures of the first two compounds have been established by x-ray diffraction analysis.

2. 4,4'-Didehydrobis-(5-methyl-2-phenyl-1,2,3-diazaphosphole) has been obtained by UV irradiation of 5-methyl-2-phenyl-1,2,3-diazaphosphole. 4,4'-Didehydrobis-(2-phenyl-5-R-1,2,3-diazaarsoles) (R = Ph, Me) are not formed under similar conditions, but have been obtained by reacting the 2-phenyl-5-R-1,2,3-diazaarsoles with methylphenyldiazomethane and cyclohexanone.

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REACTION OF AMMONIUM 1,3,2,5-DIOXABORATAPHOSPHORINANES WITH ELECTROPHILIC REAGENTS

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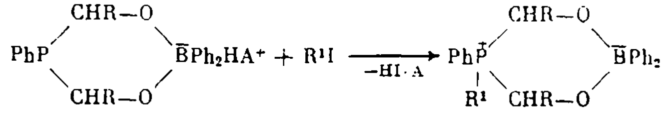
Ammonium 1,3,2,5-dioxaborataphosphorinanes and their derivatives contain a cation having a labile hydrogen atom [1-3], which facilitates reactions with electrophilic reagents involving direct participation of the labile hydrogen atom. In this work alkyl halides, diphenylchlorophosphine, formaldehyde and ethylene oxide were used as electrophilic reagents.

Reaction of N-methylmorpholinium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane (I) and of triethylammonium 2,2,5-triphenyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphorinane (II) with methyl and ethyl iodides proceeds at ~20°C to form 2,2,5-triphenyl-5-methyl- (III) and 2,2,5-triphenyl-5-ethyl-4,6-dimethyl-1,3,2,5-dioxaborataphosphoniarinanes (IV), respectively



(I), (II)
$R = H$, $A = MeN(CH_2CH_2)_2O$(I)
$R = Me$, $A = Et_3N$(II)

(III), (IV)
$R = H$, $R^1 = Me$(III)
$R = Me$, $R^1 = Et$(IV)

2,2,5,5-Tetraphenyl-4,6-dimethyl-1,3,2,5-dioxaborata-phosphoniarinane (V) was obtained under the same conditions from (II) and diphenylchlorophosphine. Apparently in the first step a bipolar ion is formed which has a diphenylphosphine group as substituent at the phosphorus atom. Subsequent enlargement of the ring, charge transfer to the second phosphorus atom, and contraction of the ring proceed due to the expulsion of $(PhP)_n$

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