2. The acidolysis of trimethylamine-3-borahomoadamantane gave cis-5-ethyl-1,3-dimethylcyclohexane.

3. 3-Homoadamantanol was synthesized by the carbonylation of tetrahydrofuran-3-borahomoadamantane with CO.

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SYNTHESIS AND STERIC STRUCTURE OF 5-PHENYL-1,3,5-DIOXAPHOSPHORINANE AND ITS DERIVATIVES

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At the present time it may be considered as established that a Ph on the P atom in phosphorinanes is found preferably in the equatorial orientation. It was shown that in the equilibrium of the conformers of 1-phenylphosphorinane [1] at −80°C and 1-phenyl-4-tert-butylphosphorinane [2] at 140° the equatorial orientation of the Ph predominates (respectively 65 and 55%). These data also testify that the dependence of the position of the equilibrium on the temperature is negligible. As in the case of substituted cyclohexane and 5-substituted 1,3-dioxanes, in phosphorinanes the orientation of a Ph on the P atom is determined by the enthalpy factor. Analogous results were obtained when the 1-phenylphosphorinan-4-ones [3, 4] and their oxides and sulfides [3, 5] were studied.

The determining effect of the enthalpy factor on the orientation of substituents on the C and P atoms in six-membered rings made it possible to propose that when going from 1-phenylphosphorinane to 5-phenyl-1,3,5-dioxaphosphorinane the same effect will be observed as when going from phenylcyclohexane to 5-phenyl-1,3-dioxane [6]. To check this assumption

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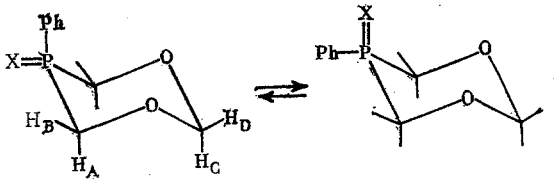
TABLE 1. Parameters of ^1H and ^{31}P NMR Spectra of (I)-(III) in Solutions (δ, ppm, J, Hz)

Compound	X	δ ^{31}P (solvent)	—OCH_2P—					—OCH_2O—				
			δ_A	δ_B	$^2J_{PA}$	$^2J_{PB}$	$-^2J_{AB}$	δ_C	δ_D	$^4J_{PC}$	$^4J_{PD}$	$-^2J_{CD}$
(I)	UEP	38 (C_6H_6)	4,33	4,49	16,7	9,3	14,0	5,10	4,72	0,0	1,4	7,0
		(CH_3CN)	4,73	4,83	6,0	14,9	14,0	5,03	5,03	—	—	—
(II)	O	−6 (C_6H_6)	3,93	4,12	−2,7	−9,8	14,0	4,73	4,20	2,1	2,8	6,2
		(CCl_4)	4,25	4,35	−5,3	−7,7	14,0	5,02	4,71	2,2	2,8	6,2
(III)	S	−8 (CCl_4)	4,00	3,82	−6,8	0,0	14,0	4,76	4,37	1,8	2,0	6,0
		(CH_3CN)	4,64	4,44	−12,4	−4,5	14,0	5,08	4,96	2,0	2,1	6,0

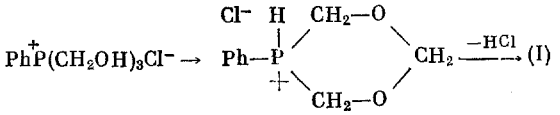
we obtained 5-phenyl-1,3,5-dioxaphosphorinane (I) and its derivatives and studied their steric structure.



X = unshared electron pair (UEP) (I), O (II), S (III).

The synthesis of (I)-(III) encounters great difficulties [7]. Only the preparation of a 5-alkyl-5-oxo-1,3,5-dioxaphosphorinane has been described by heating trimethylolphosphine with paraform at 180° in vacuo [8]. Attempts to obtain (I)-(III) by heating the appropriate diols and trimethylolphosphonium chloride with paraform at 180° or in benzene, with azeotropic distillation of the water, in the presence of p-toluenesulfonic acid or BF_3 etherate ended in failure, and here the reactants were recovered unchanged. Acetylation of the diols with a mixture of AcOH and Ac_2O gave the acetates [9]. Replacing the paraform by acetaldehyde, isobutyraldehyde or benzaldehyde failed to affect the reaction course.

Compound (I) was obtained in low yield as the hydrochloride by the vacuum-distillation of trimethylolphenylphosphonium chloride and had a signal with δ 8 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Neutralization of the hydrochloride with aqueous alkali solution led to (I). The structure of (I) was confirmed by elemental analysis, by the absence of absorption in the 3000-3600 cm^{-1} region in the IR spectrum, by one signal with δ 38 ppm in the ^{31} P NMR spectrum, and by a characteristic PMR spectrum.



Compounds (II) and (III) were respectively obtained from (I) by oxidation with H_2O_2 and by the addition of sulfur.

The steric structure of (I)-(III) was determined employing the PMR and dipole moment (DM) methods. The ^1H and ^{31}P NMR spectral data (Table 1) show that the splitting of the signals of the methylene protons of compounds (I)-(III) in various solvents corresponds to a spectrum of the $(AB)_2CDX$ system, where A and B are the axial (a) and equatorial (e) protons in the 4 and 6 positions; C and D are the protons in the 2 position; X is the nucleus of the P atom. The nonequivalence of the AB methylene protons testifies to the fact that the six-membered rings are found predominantly in the chair conformation [10]. The D protons have $^4J_{PH_D}$ = 1.4-2.8 Hz and are equatorial according to the W rule [11] (Fig. 1).

The position of the conformation equilibrium was determined from the average, and that taken from model compounds, SSCC of proton A with the nucleus of the P atom. As a model of the conformation of (I) with an *a*-orientation of the Ph we took the corresponding stereoisomer of 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane ($^2J_{PH_A}$ = 22 Hz [7]), and as a model of the conformation with an e-orientation we took 5-phenyl-1,3-dibenzyl-1,3,5-diazaphosphorinane ($^2J_{PH_A}$ = −6.3 Hz [12]). Calculation disclosed that in benzene the fraction of conformation with an *a*-orientation of the Ph on the P atom is 72%. A comparison of

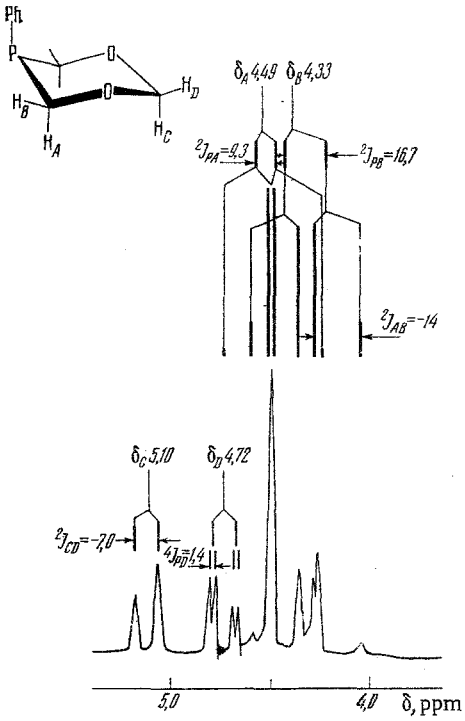


Fig. 1. PMR spectrum of (I) in C_6H_6.

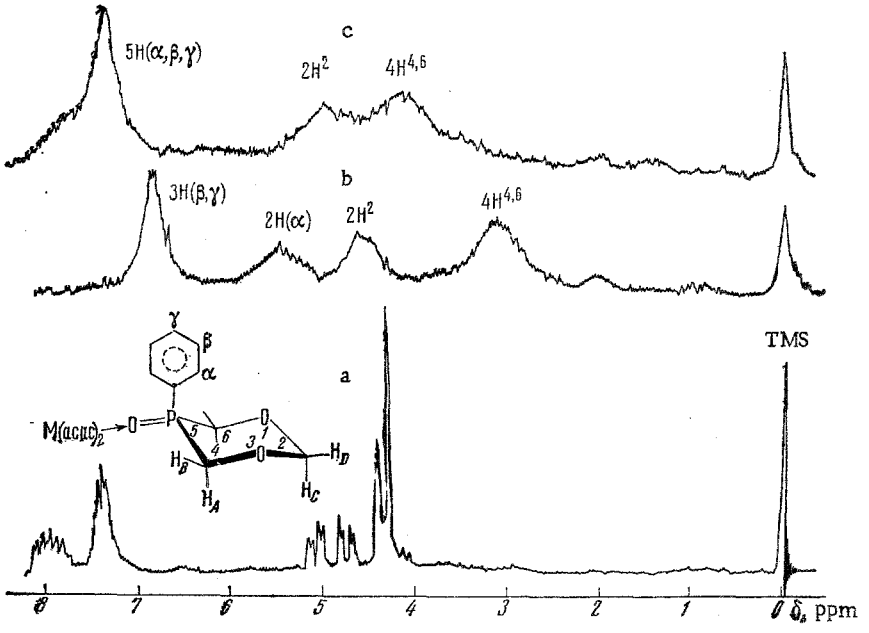


Fig. 2. PMR spectrum of (II) in CCl_4: a) 0.246 mole/liter; b) with the addition of $Co(acac)_2$, $[Co^{2+}]/[L] = 0.25$; c) with the addition of $Ni(acac)_2$, $[Ni^{2+}]/[L] = 0.25$.

the SSCC of proton A with the nucleus of the P atom of (II) and (III) with the SSCC of the corresponding stereoisomers of 5-phenyl-5-oxo-2,4,6-trimethyl-1,3,5-dioxaphosphorinane ($^2J_{HAP=Oe} = 0$, $^2J_{HAP=O\alpha} = 10$ Hz) and 5-phenyl-5-thio-2,4,6-trimethyl-1,3,5-dioxaphosphorinane ($^2J_{HAP=Se} = 6.8$, $^2J_{HAP=S\alpha} = 13.4$ Hz [7]), reveals that the conformers with an e-orientation of the P=O and P=S bonds predominate in the equilibrium.

To confirm the structure of (II) we studied the effect of the paramagnetic complexes of the nickel and cobalt acetylacetonates on the spectra (Fig. 2). A paramagnetic shift of the lines in the ^1H and ^{31}P NMR spectra is observed when the ratio of the molar concentra-

tions of the complex and (II) = 1:4. This shift is due to transfer of the spin density to the P atom, which is related to the coordination of the paramagnetic complexes at the phosphoryl oxygen [13]. The values of the pseudocontact shifts in the labile complexes of $Co(acac)_2$ with (II) made it possible to determine that the phosphoryl group in (II) is found in the e-position [14].

The dipole moment of (I) in benzene at 20° is equal to 1.96 D. The calculated DM values for the conformers with an e- and an a-orientation of the Ph on the P atom are respectively equal to 2.65 and 0.77 D. The geometric parameters and the bond polarities needed to calculate the DM were taken from [15]. A comparison of the experimental and calculated DM values shows that in the conformation equilibrium of (I) the conformer with an a-orientation of the Ph on the P atom predominates.

The dipole moments of (II) and (III) were determined in CCl_4 at 20° and proved to be respectively equal to 2.60 and 2.84 D. The calculated DM values are 2.78 and 3.20 D in the case of the e-orientation, and 5.61 and 6.03 D in the case of the a-orientation of the P=O and P=S bonds. A comparison of the experimental and calculated DM values leads to the conclusion that both compounds are found in the chair conformation with an e-orientation of the phosphoryl and thiophosphoryl groups. The results of discussing the NMR spectra and the DM are in agreement.

As a result, when going from 1-phenylphosphorinanes and their derivatives to the 5-phenyl-1,3,5-dioxaphosphorinanes and their derivatives the equilibrium is shifted toward the conformer with an a-orientation of the Ph on the P atom. The rule has a general character for the tri- and tetracoordinated P atom, and is analogous to that observed when going from substituted cyclohexanes to the 5-substituted 1,3-dioxanes. This confirms the fact that the reactions of the phenyl on the C and P atoms in the given systems have the same nature. The enthalpy factor is determining. The syn-axial reactions of Ph with the O atoms probably bear an attractive character.

EXPERIMENTAL

The PMR spectra were recorded on a Varian T-60 spectrometer (60 MHz, 34.5°), using the signal of the solvent as the internal standard. The ^{31}P NMR spectra were recorded on a KGU-4 NMR spectrometer (10.2 MHz), with noise decoupling from the protons at a frequency of 25.2 MHz. The samples represented 5 vol. % solutions in the indicated solvents (see Table 1).

The dipole moments were determined as described in [14]. The coefficients of the calculation equations were: X = UEP, α = 2.4478, γ'' = 0.1008; X = O, α = 7.2990, γ'' = 0.5089; X = S, α = 8.3714, γ'' = 0.8715.

Tri(hydroxymethyl)phenylphosphonium chloride was obtained as described in [9] in 90% yield, mp 76° (from methanol), δ ^{31}P − 20 ppm (CH_3OH).

5-Phenyl-1,3,5-dioxaphosphorinane (I). When 7.1 g (0.003 mole) of tri(hydroxymethyl)-phenylphosphonium chloride was subjected to vacuum distillation, the salt began to decompose at 150° (bath) and water distilled, and then at 200-210° (0.1 mm) we collected 2.5 g (38% yield) of a viscous oil, bp 110-120° (0.1 mm), δ ^{31}P 8 ppm. The oil was dissolved in 10 ml of benzene and then, with stirring, 5 ml of 1 N KOH solution was added to pH 9-10, after which the benzene layer was separated and washed with water until neutral. The benzene was removed in vacuo and the residue was distilled to give 1.2 g (22%) of (I), bp 95-98° (0.1 mm), n_D^{20} 1.5989, δ ^{31}P 40 ppm. Found: C 59.40; H 6.09; P 17.09%. $C_9H_{11}O_2P$. Calculated: C 59.32; H 6.09; P 17.01%.

5-Phenyl-5-oxo-1,3,5-dioxaphosphorinane (II). With water cooling, to a solution of 1.2 g (0.006 mole) of (I) in 5 ml of CH_3CN was added the calculated amount of 24% H_2O_2 solution. The volatile components were removed in vacuo and the residue was recrystallized from benzene to give 0.7 g (54%) of (II), bp 150-152° (0.1 mm), mp 124°, δ ^{31}P − 6 ppm (C_6H_6). Found: C 54.50; H 5.80; P 15.52%. $C_9H_{11}O_3P$. Calculated: C 54.53; H 5.60; P 15.64%.

5-Phenyl-5-thio-1,3,5-dioxaphosphorinane (III). To a solution of 1.05 g (0.006 mole) of (I) in 5 ml of CH_3CN was added an excess of powdery sulfur. The evolution of heat was observed. After 1 h the mixture was filtered and evaporated in vacuo. We obtained 0.87 g (71%) of (III), mp 113°, δ ^{31}P − 8 ppm (CH_3CN), found: C 50.20; H 4.86; P 14.22%. $C_9H_{11}PO_2S$. Calculated: C 50.46; H 5.18; P 14.47%.

EXPERIMENTAL

In the conformational equilibrium of 5-phenyl-1,3,5-dioxaphosphorinane, its oxide, and its sulfide in a nonpolar solvent, theconformer with an axial orientation of the phenyl moiety on the phosphorus atom predominates.

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