STRUCTURE OF o-HYDROXYARYLOXY-BIS(o-ARYLENEDIOXY)-PHOSPHORANES AND THEIR ACID PROPERTIES

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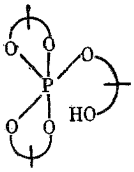
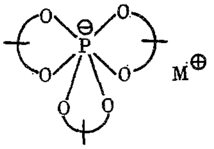
In the field of penta- and hexacoordinated phosphorus compounds, which has been intensively developed in recent years, much attention has been focused on the question of the structure of the products of reaction of PCl_5 and other pentacovalent orthophosphates with excess pyrocatechol. This question has been the subject of many investigations in which the authors have arrived at contradictory conclusions about the structure of the three major reaction products: o-hydroxyphenoxy-bis-(o-phenylenedioxy)phosphorane (Ia), tris-(o-phenylenedioxy)phosphorate anion (IIa), and o-phenylenedioxy-bis-(di-o-phenylenedioxy)phosphorane (IIIa)



(I)



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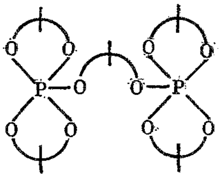

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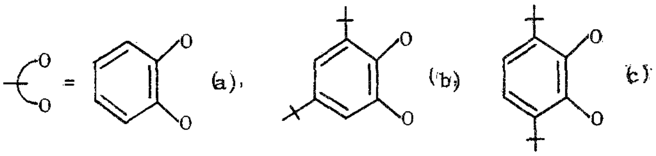
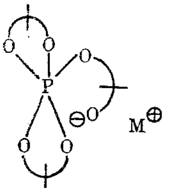


In most work, the presence of phosphorane (Ia) has been judged only from the ^{31}P NMR chemical shift $\delta = -29$ ppm (benzene). In a number of cases, its intermediate formation has been assumed in the chain of conversions leading to (IIa) [1-4].

With regard to the structure of compound (IIa) in the crystalline state with the cation $M^+ = NEt_3H^+$ or $Me_2NH_2{}^+$ as compounds with a hexacoordinated phosphorus atom, all the authors are in agreement and it has been conclusively demonstrated by the x-ray diffraction method [5]. As far as the structure of this compound in solutions in neutral solvents is concerned, analysis of the ^{31}P NMR data ($M^+ = NEt_3H^+$) is definitely evidence in favor of structure (IIa) [6], but a proposal has also been made concerning structure (IVa) with rapid resonance migration of the anionic charge along all six oxygen atoms, which thus become equivalent [7]. Furthermore, structure (IVa) has been assumed as an intermediate upon formation of (IIa) from (Ia) [1]



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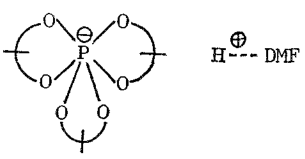

(V)

In weakly basic solvents (DMF), structure (IIa) has been considered, where M^+ is the protonated solvent molecule [1], as well as structure (Va), the so-called free acid, without discussing the character of the H^+...DMF bond [2]. In solvents with stronger basic

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TABLE 1. ^{31}P NMR Spectral Data for Phosphoranes (I) and Phosphorates (II)

Compound	δ, ppm	Compound	δ, ppm
(Ib)	−27,8; −27,1*(benzene)	(IIb)	−83,69; −83,73* (CH_3CN)
(Ic)	−35,1 (toluene)	(IIc)	−83,43 (CH_3CN)

*Mixtures of two stereoisomers.

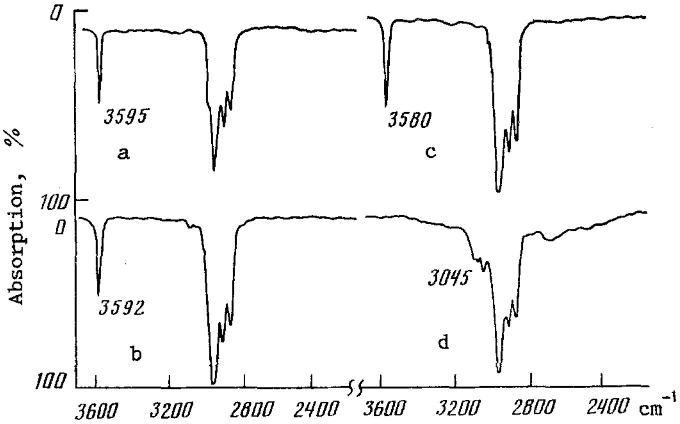
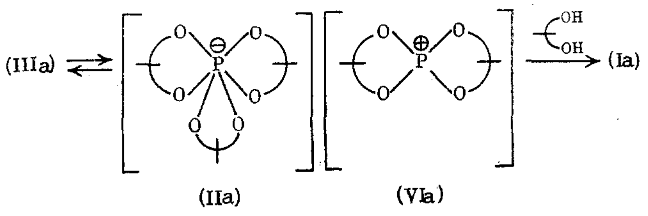


Fig. 1. IR spectra: phosphorane (Ic) in CCl_4, 0.05 moles/liter (a) and in the solid state (suspension in hexachlorobutadiene) (b); phosphorane (Ib) in CCl_4, 0.1 moles/liter (c); phosphorate (IIb) in the solid state (suspension in hexachlorobutadiene) (d).

properties (Et_3N), all the authors assume structure (IIa) when $M^+ = BH^+$.

Structure (IIIa) in the crystalline state has been confirmed by the x-ray diffraction method [8], but in chloroform solutions structure (Ia) has been assumed [1]. In [4] it is shown that in neutral solvents we observe the equilibrium between (IIIa) and the ion pair (IIa)·(VIa)



In this case, the chemical shift in benzene at 25°C in the ^{31}P NMR spectrum, equal to −31 ppm, is considered as a value averaged as a result of rapid exchange, for a chemical shift for the (IIa) anion of δ = −84 ppm and for the (VIa) cation of δ = 12.5 ppm. Upon addition of pyrocatechol to the equilibrium mixture, all the participating species are converted to (Ia) with δ = −29 ppm.

In this work we have obtained crystalline phosphoranes (Ib) and (Ic); we have studied the vibrational, electronic, and NMR spectra of these compounds and products of their reaction with nitrogen bases. The phosphoranes (Ib) and (Ic) were synthesized upon boiling in o-xylene a mixture of PCl_5 and the corresponding pyrocatechol taken in the stoichiometric ratio (1).

In the ^{31}P NMR spectra of phosphoranes (Ib) and (Ic) in benzene, the signal is found in the region −28 to −35 ppm (Table 1), characteristic for oxygen compounds of five-coordinate phosphorus [4]. In the IR spectra of these substances in the solid state and in CCl_4 solutions (Fig. 1), there is an absorption bands from the phenol hydroxyl at 3580 (Ib) and

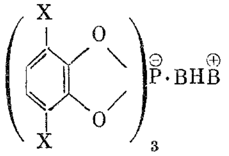
3595 cm^{-1} (Ic). These spectral data already allow us to assign structure (I) to phosphorane; accordingly, in the UV spectrum of phosphorane (Ib), we observe two bands for the $\pi-\pi^*$ transition of the phenyl rings at 279.5 and 274 nm; and the low-frequency band with respect to its position corresponds exactly to the 279.5 nm band in the spectrum of di-tert-butyl-pyrocatechol. We [9] have also carried out x-ray diffraction analysis of phosphorane (Ic), which has confirmed structure (I).

Upon reaction of phosphoranes (I) with bases (such as NEt_3), the phosphorates (II) are formed ($M = NEt_3H^+$) [2, 4, 6]. In order to establish their structure, we used ^{31}P NMR, IR, and UV spectra.

In the NMR spectra, the phosphorates (IIb) and (IIc) which we studied ($M^+ = NEt_3H^+$), the phosphorus signal is found in the −83 ppm region (see Table 1), characteristic for oxygen compounds of six-coordinate phosphorus (structure II) [6]. In the IR spectra of these substances (see Fig. 1), in the region of the CH vibrations the 2180 cm^{-1} band of the original triethylamine is missing, and a band appears in the high-frequency region at 3045 cm^{-1} from the alkyl-substituted ammonium salts [10]. Furthermore, in the IR spectrum of phosphorate (II) ($M^+ = NBu_2H_2{}^+$) a band is present from the bending vibrations of the $N_2{}^+$ groups, $\delta NH_2{}^+ =$ 1630 cm^{-1}, which indicate its ionic structure.

In the UV spectrum of phosphorate (IIb), there is a single band at 296.5 nm which is consistent with structure (II), in which all the phenyl rings are equivalent. On the whole, the spectral data obtained confirm the ionic structure of the phosphorates (II) with six-coordinate phosphorus both in the solid state and in solutions. Comparing the structures of phosphoranes (I) and phosphorates (II) ($M^+ = NEt_3H^+$), we may see that both partners of the acid–base interaction have acid residues with different structure; i.e., the process of proton transfer here is accompanied by the phosphorane–phosphorate conversion.

A characteristic feature of the studied systems is the ease of the phosphorane–phosphorate conversion upon action of bases of different strength; this apparently is the reason for the contradictory ideas concerning their structure. The behavior of phosphorane (Ic) in DMF is significant; in the ^{31}P spectrum, we observe a signal at −83 ppm, which indicates the presence in the solution of six-coordinate phosphorus. Crystals have been isolated from the solution, whose elemental analysis and ^{31}P NMR spectra indicate structure (VII)

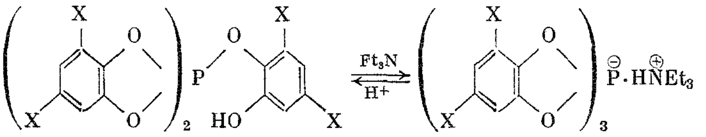


(VII)

X = *t*-Bu; B = DMF.

Consequently, when phosphorane (Ic) is dissolved in DMF, proton transfer occurs between the phenol hydroxyl and the solvent with formation of the basic phosphorate DMF (VII), in which the proton is bonded to a strong complex of the BHB^+ type with solvent molecules.

We have studied in more detail the acid–base properties of phosphoranes (I). We have carried out direct and back titration of phosphorane (Ib) in $CHCl_3$ solutions of triethylamine and perchloric acid respectively. We followed the position of the equilibrium from the absorption band of phosphorane (Ib) and the phosphorate salt (IIb) in the UV spectra of the reaction mixtures (Figs. 2 and 3). These bands on curves with different ratios of components intersect at the isosbestic points, which indicates the presence of the equilibrium



(1)

X = *t*-Bu.

With strong organic bases (for example, NEt_3), the equilibrium as a whole is shifted to the right. For weaker bases (such as dimethylaniline), even when present in excess, we can observe a phosphorane–phosphorate equilibrium in the solutions. We have investigated the PMR spectra of phosphorane (Ib) with $Ph^{15}N(CD_3)_2$ in CDF_2Cl at −100 to −30°C.* In the

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*The PMR spectra were taken by N. S. Golubev.

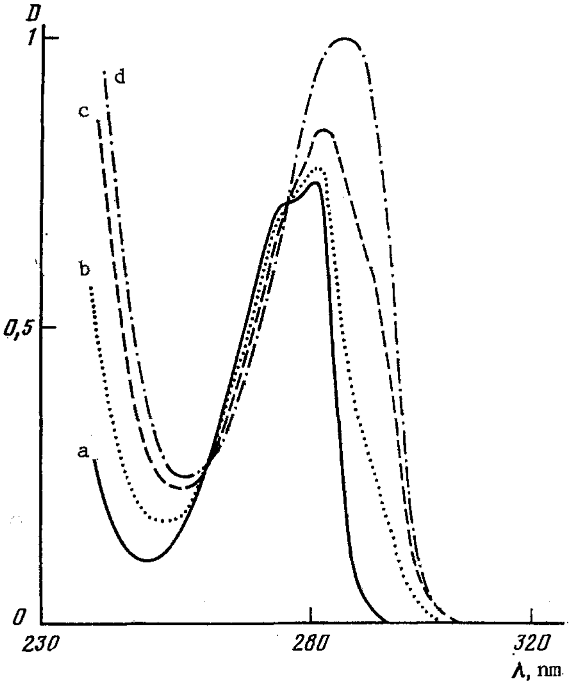


Fig. 2. UV spectra of phosphorane (Ib) in $CHCl_3$, 10^{-3} moles/liter, for successive addition of NEt_3: a) 0; b) 25; c) 50; d) 75% (direct titration).

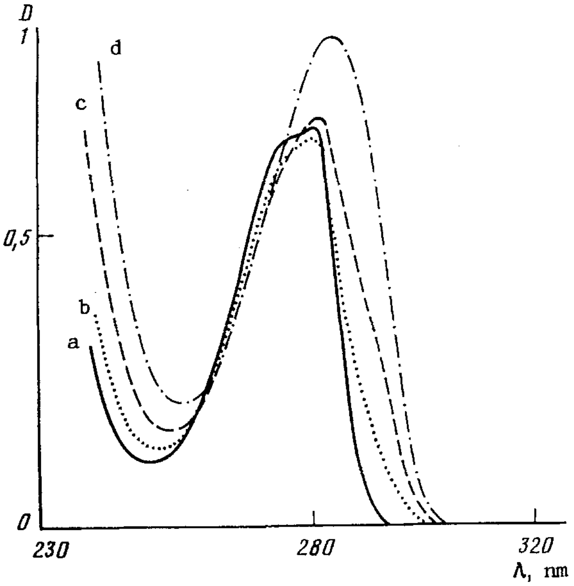
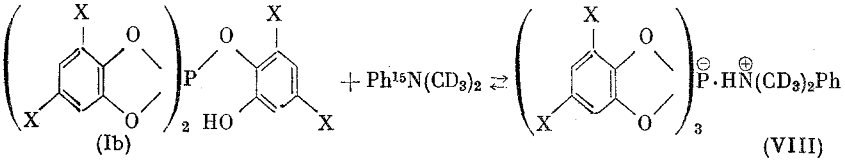


Fig. 3. UV spectra of phosphorate (IIb) in $CHCl_3$, 10^{-3} moles/liter, for successive addition of perchloric acid solution in CH_3CN: a) 100; b) 75; c) 50; d) 25% (back titration).

spectrum of the reaction mixture, there are signals from the protons of the OH group in phosphorane (Ib), δ = 12.6 ppm, and from the $^{15}NH^+$ group in phosphorate (VIII), δ = 5.2 ppm. For wide variation in temperature and component ratios, in the spectra we do not observe signals from protons of any other forms (such as the phenolate structure (IV)) which might participate in exchange processes. Thus, the reaction of phosphorane (Ib) with $Ph^{15}N(CD_3)_2$ in inert media may be represented by the equilibrium scheme



(Ib) (VIII) (2)

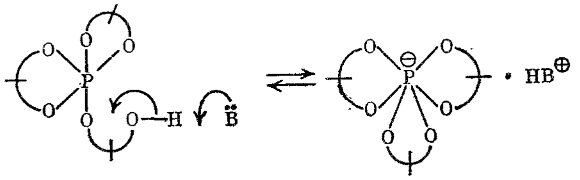
The limiting low values of the chemical shift of the signal from the ^{15}NH group (δ = 5.2 ppm) shows that the $^{+}$NH group in the phosphorate (VIII) does not participate in formation of H bonds (with the aniline or the solvent).

Then we estimated the acidity of phosphorane (Ic) by titration in nitromethane by diphenylguanidine (DPG) (for the technique, see [11]). The value obtained of $pK_a(CH_3NO_2)$ = 10.5 shows that the "acidity of the phenol hydroxyl" is ∿13 orders of magnitude higher than the acidity of the phenol (pK_a ∿ 23), and in strength it corresponds to substituted acetic acids [11].

Such an unusually high "acidity of the phenol hydroxyl" may be understood if we represent the neutralization equation in the general form

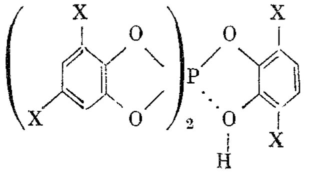
$$AH + B \rightleftarrows {}^{*}A^{-} + HB^{+} \tag{3}$$

Here AH is a weak pseudoacid of the phenol type (structure (I)); $^{*}A^{-}$ is the phosphorate anion (II), which may be considered as the anion of a true acid, existing only in the form of the salt. Thus abstraction of the proton from the phenol phosphorane (the pseudoacid) does not lead to the phenolate anion, but rather is accompanied by formation of the oxygen—phosphorus σ bond in a single elementary event



This reaction leads to stabilization of the anion and accordingly to an increase in the strength of the phenol acid.

The ease of cyclization in the studied systems may be connected with the conformational rigidity of the phenoxyl fragment in the phosphorane molecule, which develops as a result of the weak coordination interaction between the phosphorus atom and the oxygen atom of the hydroxyl group. Structurally, this is apparent in the shortened P...O distance (3.231 Å) compared with the sum of the van der Waals radii of these atoms (3.30 Å) [9]



Such an interaction is also apparent in the low-frequency shift ($\Delta\nu OH$ = 40-50 cm^{-1}) of the bands from the OH groups in the IR spectra of phosphoranes (Ib) and (Ic) (Fig. 1) compared with the spectra of the corresponding pyrocatechols; both in CCl_4 and in the crystal, the position of the νOH bands does not change. This band shift cannot be connected with formation of H bonds: in the crystal of phosphorane (Ic), the OH group does not have shortened intermolecular contacts [9].

We have estimated the position of equilibrium (3) for reaction of phosphorane (Ib) in CCl_4 and $CHCl_3$ with different nitrogen bases, the strength of which varied over broad limits of $pK_a(H_2O)$ = 4-11. The position of the equilibrium was established from the change in intensity of the band νOH = 3580 cm^{-1} for phosphorane (Ib) in the IR spectra of the reaction mixtures for a 1:1 ratio of components.

Reaction of phosphorane (Ib) with the strong bases triethylamine, dibutylamine, morpholine, imidazole, and 2,6-lutidine (pK_a = 6.2-11.2) leads to formation of phosphorates (II) in quantitative yield ($AH + B \rightarrow {}^{*}A^{-} + HB^{+}$). In the case of the weaker bases dimethylaniline (pK_a = 5.1) and p-bromodimethylaniline (pK_a = 4.23), in the solutions we observe equilibrium (3), and the reaction mixtures in CCl_4 contain respectively ∿20% and ∿60% phosphorane (Ib).

We should emphasize that for weak bases equilibrium (3) is very dynamic and its position strongly depends on the solvent. A graphic illustration of this is the behavior of phosphorate DMF (VII) in different media. This salt in DMF retains its phosphorate structure (VII): in the ^{31}P NMR spectrum there is a single signal at −83.6 ppm. However, in $CHCl_3$, the equilibrium is completely shifted toward formation of the original phosphorane (Ic) and DMF. In the ^{31}P NMR spectrum of this solution, we observe a single signal at −35 ppm for phosphorane (Ic); in the IR spectrum, accordingly we see the characteristic bands of the phenol hydroxyl $\nu OH = 3592\ cm^{-1}$ of phosphorane (Ic) and the carbonyl group $\nu C{=}O = 1675\ cm^{-1}$ of the DMF molecules. It is interesting that in acetonitrile solution, in the ^{31}P NMR spectrum we can observe signals from both equilibrium forms: the phosphorate (VII) ($\delta^{31}P$, −80.1 ppm) and the phosphorane (Ic) ($\delta^{31}P$, −28.4 ppm), and with approximately equal intensity.

The presence of a dynamic phosphorane—phosphorate equilibrium shows that in the phosphorate anions, ring opening occurs rather easily. This result may be connected with delocalization of the negative charge in the anion on the oxygen atoms of the phosphorus octahedron. Evidence for such delocalization of the negative charge comes from the position of the signal in the ^{31}P NMR spectra of the series of phosphorate anions with different numbers of oxygen atoms [6]: as the number of oxygen atoms in the phosphorate anions increases, a downfield shift occurs in the signal, which may be connected with delocalization of the negative charge on the oxygen atoms of the phosphorate anions.

Thus, the characteristic feature of the acid—base properties of phosphoranes (I) which has given rise to such contradictory ideas concerning their structure involves the fact that the process of proton transfer to the base is accompanied here by the synchronous cyclization reaction. This new type of acid—base interaction, involving the fact that the hydroxyl group in the phosphorane molecule, being a proton-donor of the phenol type, displays enhanced acidity and with different bases yields products of complete proton transfer. In this case, salts are formed with anions of the phosphorate type rather than with phenolate anions.

EXPERIMENTAL

The studied compounds were synthesized under a dry inert atmosphere; the solvents were dehydrated immediately before the run.

Bis(3,5-di-tert-butylphenylenedioxy-1,2)-2-hydroxy-3,5-di-tert-butyl-phenoxyphosphorane (Ib). A mixture of 7.1 g (0.03 moles) 3.5-di-tert-butylpyrocatechol, 2.2 g (0.01 moles) PCl_5, and 5 ml o-xylene were boiled for 20 min; 5 ml of o-xylene were added to the mixture; the mixture was cooled, the precipitated crystals were filtered off and recrystallized from xylene. We obtained 3.3 g (50%) phosphorane (Ib), m.p. 170-188°C. Found: C 72.8; H 8.7; P 4.6%. $C_{42}H_{61}O_6P$. Calculated: C 72.8; H 8.9; P 4.5%.

Bis(3,6-di-tert-butylphenylenedioxy-1,2)-2-hydroxy-3,6-di-tert-butyl-phenoxyphosphorane (Ic). A mixture of 4.0 g (0.018 moles) 3,6-di-tert-butylpyrocatechol, 1.2 g (0.006 moles) PCl_5, and 7 ml o-xylene was boiled for 5 h. The residue precipitated upon cooling was filtered off and recrystallized from toluene. We obtained 1.8 g (43%) phosphorane (Ic), m.p. 193-194°C, compare with [12].

Crystalline Complex (Ic)·ADMF. A mixture of 4.5 g (0.02 moles) of 3,6-di-tert-butylpyrocatechol, 1.0 g (0.005 moles) PCl_5, and 3 ml o-xylene was boiled for 4 h; the solvent was evaporated under vacuum; the residue was dissolved upon boiling in 5.5 ml DMF. The residue precipitated upon cooling was filtered off and recrystallized from DMF. We obtained 2.1 g (50%) (Ic)·2DMF, m.p. 160-164°C. Found: C 68.6; H 9.0; P 3.7%. $C_{48}H_{75}O_8N_2P$. Calculated: C 68.7; H 9.0; P 3.7%.

The IR spectra were taken on the UR-20 spectrometer in the solid state (KBr, petrolatum, hexachlorobutadiene) and in solutions of CCl_4 and $CHCl_3$ with concentration 0.05-0.1 moles/liter.

The UV spectra were taken on the Hitachi EPS-034 spectrometer in $CHCl_3$ with concentration 10^{-3} moles/liter; direct titration was carried out with successive addition of NEt_3 to the solution of phosphorane (Ib) in $CHCl_3$; back titration was accomplished with successive addition to this mixture of a solution of perchloric acid in CH_3CN.

The PMR spectra were taken in CDF_2Cl at the temperatures −100 to −30°C on the Jeol C-60 HL spectrometer with concentrations $(3\text{-}20)\cdot 10^{-3}$ moles/liter. The $^{31}P\{H^1\}$ NMR spectra were taken on the Bruker HX-90 spectrometer (36.43 MHz) with concentrations 0.1 moles/liter, 30°C, external standard 85% H_3PO_4; solvents were benzene for the phosphoranes and CH_3CN for the phosphorates.

CONCLUSIONS

1. We have obtained crystalline phosphoranes with o-hydroxyphenyl substituent and we have studied their vibrational, electronic, and NMR spectra, and also the spectra of the products of their reaction with nitrogen bases.

2. The molecular structure with a five-coordinate phosphorus atom corresponds to the investigated phosphoranes; and the ionic structure with a six-coordinate phosphorus atom corresponds to the phosphorates.

3. A new type of acid–base interaction has been established, connected with the fact that the process of proton transfer is accomplished by phosphorane–phosphorate conversions; in this case the hydroxyl group in the phosphorane molecule displays enhanced acidity, and yields products of complete proton transfer with different bases.

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