

## "WANDERING" VALENCY IN ORGANOPHOSPHORUS FREE RADICALS

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**Abstract** - Phosphorus-containing radicals of the type

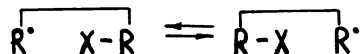
$\left[ \begin{array}{c} \text{O} \\ \diagup \\ \text{P} \\ \diagdown \\ \text{O} \end{array} \right] \cdot$  where  $\text{O} \text{---} \text{O}$  stands for phenylenedioxy group, are described. The new radicals have been generated by photochemical addition of o-quinones to phosphorus or by photoreactions of o-quinones with hydrogen spirophosphoranes. Oxidation of corresponding o-oxySpirophosphoranes with  $\text{PbO}_2$  leads to the same radicals. The ESR spectra of the radicals obtained show a characteristic temperature dependence. Hyperfine splittings observed at low temperatures correspond to unpaired electron interactions with protons of only one aromatic ring, whereas at higher temperatures, protons of two or all the three aromatic ligands are involved. In the latter case, the radical has an octahedral symmetry on the ESR time scale, and the unpaired electron "wanders" over six oxygen atoms ("wandering valency"). The number of oxygen atoms participating in spin delocalization may be lower than 6 depending on the radical structure. The phenomenon described is a new type of phosphorotropic tautomerism. Temperature-dependent variations of the ESR spectra studied include characteristic linewidth alternations which have been used to calculate exchange frequencies. A possible mechanism of valency wandering is discussed.

New radicals have been generated by reduction of phosphorate anions containing hexacoordinate phosphorus. Salts containing these anions have been prepared from ortho-quinones and phosphorus in high yields. The properties of the new compounds are described.

The wandering valency phenomenon has also been observed with radicals containing other than phosphorus elements, such as boron, aluminium, silicon, arsenic, etc. . Temperature variations of ESR spectra of these radicals have been studied.

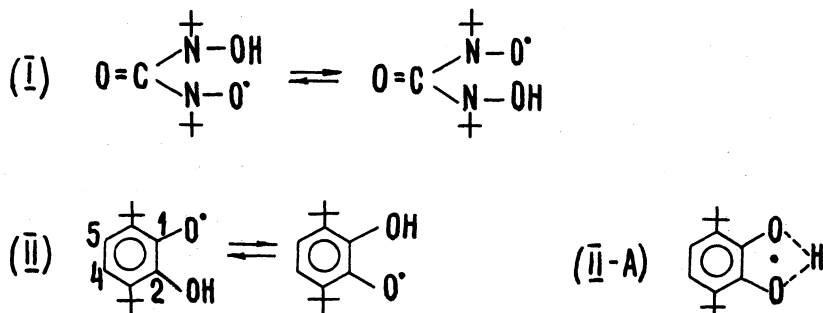
By analogy with ionotropic tautomerism, we use the term tautomerism of free radicals to describe their spontaneous and reversible isomerization:

One of the possible isomerization mechanisms is free valency and bond transfer within the radical:



The process should be regarded as intramolecular radical substitution at X. With symmetrical radicals (R is identical to R'), the equilibrium is degenerate which implies a double-well potential with two minima of the same depth.

The group X undergoing migration may be hydrogen. Aurik and Stork were the first to observe such radical H-tropy as degenerate tautomerism of iminoxyl radical (I) in 1972 [1]. Somewhat later we have studied phenoxyl radical (II) and its tautomerism [2].



(Here the symbol + is used to denote the tertial butyl group).

More recently, similar H-tropy processes in free radicals have been reported by other authors [3]. We have, however, found that many other Group II, III, IV and V elements may undergo radical shifts. Since 1976, the new types of free radical tautomerism such as borotropy, alumotropy, silicotropy and particularly phosphorotropy which is the principal subject of the present lecture, have been extensively studied in this laboratory. To give a systematic account of the problem, I will begin with H-tropy and touch upon some points concerning shifts of other elements in free radicals.

The conclusion of degenerate tautomerism in radical (II) was drawn from temperature dependence of its ESR spectrum. This contains a triplet of doublets at 60°C (Fig. 1). The doublet splitting arises from hyperfine interaction between the unpaired electron and hydroxyl proton. The triplet splitting is due to two equivalent protons which may only be the 4 and 5 ring protons. The reason for their equivalence may be twofold. Firstly, it may be a symmetrical H-bond (II-A). Secondly, fast free valency and H-atom shifts between the 1 and 2 oxygen atoms, i.e. the exchange phenomenon, may contribute.

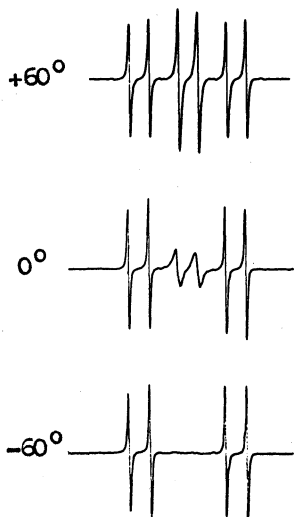
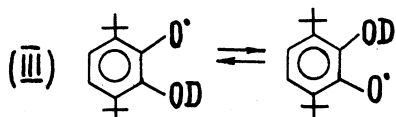


Fig. 1. ESR Spectrum of radical (II) in dioxan. At +60°: doublet,  $a_{\text{OH}} = 1.62$  oe., triplet,  $a_{\text{H(ar.)}} = 3.92$  oe. At -60°: two doublets,  $a_{\text{OH}} = 1.62$  oe.,  $a_{\text{H(4)}} = 7.74$  oe.

Temperature lowering results in broadening of the middle triplet components such that the spectrum becomes a doublet of doublets at -60°C. The small doublet splitting is due to the hydroxyl proton, whereas the larger one (7.84 oe) arises from hyperfine interaction with the ring proton positioned para- to the monovalent oxygen atom. The temperature effects mentioned are fully reversible.

The arguments for fast H-atom shifts are as follows:

1. Broadening of middle triplet components with temperature lowering, i.e. linewidth alternation, may only be caused by exchange.
2. The exchange frequency  $\nu$  calculated from signal broadening depends on the solvent nature. It decreases in solvents capable of H-bonding.
3. At sufficiently low temperatures ( $-60^{\circ}\text{C}$ ), the exchange is quenched, and the ESR spectrum corresponds to the radical with fixed free valency and OH bond positions. The hyperfine constant at  $-60^{\circ}$  has twice the value characteristic of the triplet observed at  $+60^{\circ}\text{C}$ .
4. Deuterium shift in radical (III):



is associated with a normal isotropic effect equal to that calculated from the corresponding vibrational frequencies (Table 1).

TABLE 1. Isotropic effect on exchange frequency ( $\nu_{\text{D}}/\nu_{\text{H}}$ ) in 3,6-Di-tert. butyl-2-oxyphenoxy radical.

$t^{\circ}\text{C}$	$\nu_{\text{D}}/\nu_{\text{H}}$	
	Found	Calculated
20	0.08	0.09
60	0.14	0.12
80	0.16	0.14
120	0.22	0.17

The linewidth alternation in the ESR hyperfine structure is a well known and thoroughly studied phenomenon characteristic of exchange processes. It depends on that not all the ESR lines undergo exchange broadening but only those corresponding to equal summarized nuclear spin projections.

An elaborate theory of exchange broadening of ESR lines has been worked out [4, 5] which provides a means of calculating exchange frequencies and, from their temperatures dependences, exchange kinetic parameters. Exchange may be fast, slow, or have an intermediate rate.

With fast exchange, broadening  $\Delta(1/T_2)$  is proportional to square of the initial distance between the lines involved and inversely proportional to the exchange frequency (1).

$$\Delta(1/T_2) = \mathcal{K}(\delta H_0)^2/\nu \quad (1); \quad \Delta(1/T_2) = \mathcal{K}'\nu \quad (2).$$

In the case of slow exchange, broadening is proportional to exchange frequency (2). Shifting of broadened components towards each other provides a clear indication of fast exchange. Practically no shift accompanies broadening when exchange is slow. In actual calculations based on exchange broadening, line amplitudes are usually measured. These are proportional to squares of linewidths and are easier to determine. The experimental data for radical (II) gave hydrogen and free valency migration frequency of  $5.5 \cdot 10^9 \text{ sec}^{-1}$  at  $60^{\circ}\text{C}$ .

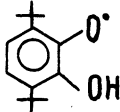
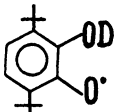
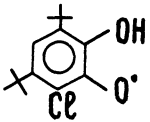
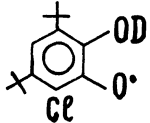
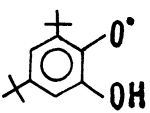
The temperature dependence of ESR spectra and linewidth alternation phenomenon have been used in the study of tautomerism of many other free radicals.

#### 1. TWO-WELL POTENTIAL SYSTEMS

The above-mentioned radical (II) and its deuterated derivative (III) provide examples of a degenerate tautomeric system having two potential wells

of equal depths. We have also studied nondegenerate systems (IV and V) involving hydrogen and deuterium shifts between two nonequivalent positions. The mean exchange frequency in these systems is lower by an order of magnitude than with (II) and (III) (Table 2).

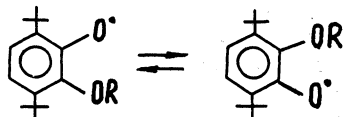
TABLE 2. Kinetic parameters of hydrogen atom and free valency shifts in radicals

№	Compound	Solvent	$\nu_{20} \text{sec}^{-1}$	$\nu^0 \text{sec}^{-1}$	$E$ kcal/mol	Ref.
II		heptane	$2,2 \cdot 10^9$	$3,3 \cdot 10^{11}$	$2,9 \pm 0,2$	[2]
III		heptane	$2,6 \cdot 10^8$	$6,0 \cdot 10^{11}$	$4,5 \pm 0,2$	[2]
IV		toluene <sup>*)</sup>	$3,8 \cdot 10^8$ $3,5 \cdot 10^8$	$4,5 \cdot 10^{11}$ $2,1 \cdot 10^{11}$	$4,1 \pm 0,5$ $3,8 \pm 0,5$	[6]
V		toluene <sup>*)</sup>	$2,9 \cdot 10^7$ $2,3 \cdot 10^7$	$5,4 \cdot 10^{11}$ $2,5 \cdot 10^{11}$	$5,7 \pm 0,5$ $5,4 \pm 0,5$	[6]
VI			no migration			[7]

<sup>\*)</sup>The parameters for direct and reverse reactions are given.

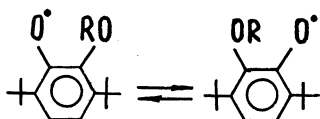
Interestingly enough, the ESR spectrum of VI does not show the typical temperature-dependence pattern. The meta- position of the hydroxyl group is, seemingly, greatly favoured over the ortho- one, and the ortho-structure can hardly be realized. Some organophosphorus radicals show a similar behaviour.

The data on tautomerism of some free radicals of the type



where R is an organic or organometallic group are listed in Table 3.

TABLE 3. Kinetic parameters of R-shifts in the system



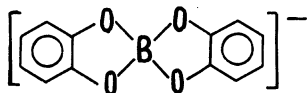
№	R	Solvent	$\nu_{20} \text{sec}^{-1}$	$\nu^{\circ} \text{sec}^{-1}$	E kcal/mol	Ref.
VII	CH <sub>3</sub>	benzene naphthalene	$0 \leq \nu \ll 10^4$	$\text{sec}^{-1}$		[9]
VIII	COCH <sub>3</sub>	benzene	$\sim 10^4$	$9,0 \cdot 10^{12}$	$11,4 \pm 1,0$	[8]
IX	Sn(CH <sub>3</sub> ) <sub>2</sub> Cl	toluene	$2,4 \cdot 10^6$	$2,4 \cdot 10^{14}$	$10,7 \pm 0,5$	[10]
X	Si(CH <sub>3</sub> ) <sub>3</sub>	pentane	$2,5 \cdot 10^6$	$1,6 \cdot 10^{13}$	$9,3 \pm 1,0$	[9]
XI	Al(Acac) <sub>2</sub> <sup>⊖</sup>	ether + toluene, 5:1	$2,5 \cdot 10^9$	$1,3 \cdot 10^{14}$	6,3	[11]
XII	Sn(CH <sub>3</sub> ) <sub>3</sub>	toluene	$\gg 10^9$	-	-	[10]

<sup>⊖</sup>) Acac stands for acetylacetonyl.

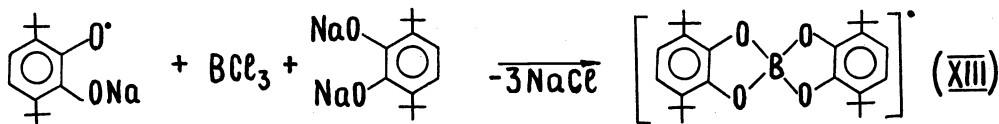
The data in Table 3 show that the methyl group is either incapable of migration or shifts at a very low frequency. The acetyl and other acyl groups migrate only slowly; the trimethylsilyl group shifts at a higher rate, and migration of the trimethylstannyl group is an exceedingly fast process. Exchange frequencies appear to increase with the extent of co-ordination undersaturation of the central atom.

## 2. FOUR-WELL POTENTIAL SYSTEMS

Here belong radicals containing a formally tetra-coordinate element as central atom such as boron or aluminium. Esters of boric acid are noted for their ability to add alcohols with the formation of complex acids [(RO)<sub>4</sub>B]. A spirocyclic pyrocatechol complex anion is known [12]:



Radical (XIII) having a similar structure shows all the characteristic features of a tautomeric system. This was obtained from the reaction [13]:



The ESR spectrum of the radical in THF is a quadruplet whose components have equal intensities (Fig. 2). The quadruplet splitting is due to interaction of the unpaired electron with the paramagnetic <sup>11</sup>B nucleus (spin of 3/2). At low temperatures (-100°C) each quadruplet component decomposes into a 1:2:1 triplet.<sup>⊖</sup> Additional broad lines appear as the sample is

<sup>⊖</sup>) In addition to that, weak lines from <sup>10</sup>B are present in the spectrum.

heated, further, they undergo narrowing. Beginning with  $+20^{\circ}\text{C}$ , each  $^{11}\text{B}$  line component splits into a quintiplet with a binomial intensity distribution.

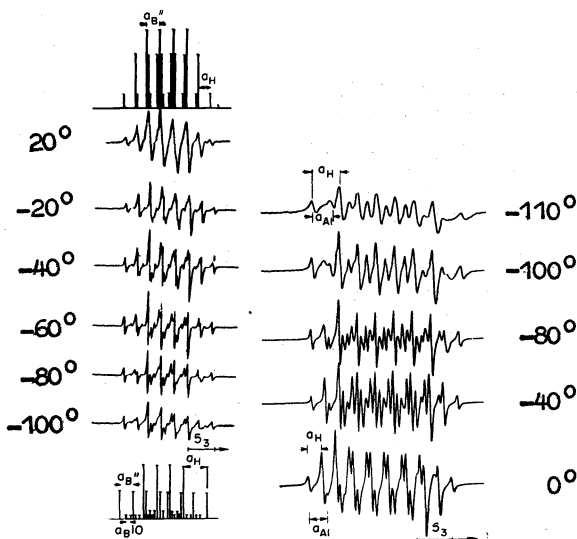


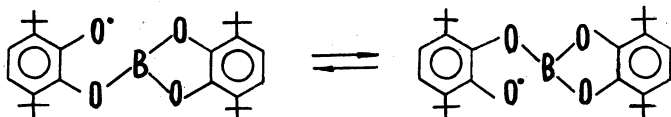
Fig. 2.

Fig. 3.

Fig. 2. ESR-spectrum of radical (XIII) in THF. Quadruplet 1:1:1:1,  $a_{\text{B}}=2,5$  oe. At  $-100^{\circ}\text{C}$ : triplet 1:2:1,  $a_{\text{H}}=4,5$  oe.; at  $+20^{\circ}\text{C}$ : quintiplet 1:4:6:4:1,  $a_{\text{H}}=2,25$  oe.

Fig. 3. ESR-spectrum of radical (XIV) in THF. Sextiplet 1:1:1:1:1:1,  $a_{\text{Al}}=2,58$  oe. At  $-110^{\circ}\text{C}$ : triplet 1:2:1,  $a_{\text{H}}=4,0$  oe.; at  $0^{\circ}$ : quintiplet 1:4:6:4:1,  $a_{\text{H}}=2,0$  oe.

The quintiplet splitting may only be due to four equivalent protons of pyrocatechol rings, viz. 4, 4', 5, and 5'. The triplet splitting observed at  $-100^{\circ}\text{C}$  is indicative of the presence of only two equivalent protons responsible for splitting of the signal. Their equivalence may be explained by fast intraligand exchange:



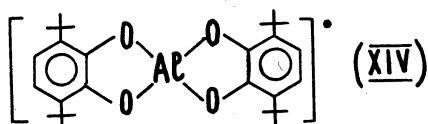
At higher temperatures, interligand exchange contributes.<sup>\*)</sup>



The fact that fast exchange proton splitting,  $a_{\text{H}}$ , is equal to 2.25 oe (quintiplet), whereas intraligand exchange gives rise to a 4.5 oe, i.e. twice as large, splitting (triplet), confirms the suggestion of fast exchange involving all the four oxygen atoms at  $20^{\circ}\text{C}$ . The corresponding exchange frequency calculated from linewidth data is equal to  $\nu_{\text{exch}} = 2 \cdot 10^9$  sec $^{-1}$  at  $20^{\circ}\text{C}$ . We thus deal here with the phenomenon of "wandering" valency: at temperatures higher than  $20^{\circ}\text{C}$ , free valency runs over all the four oxygen atoms at a frequency of  $10^9$  sec $^{-1}$ .

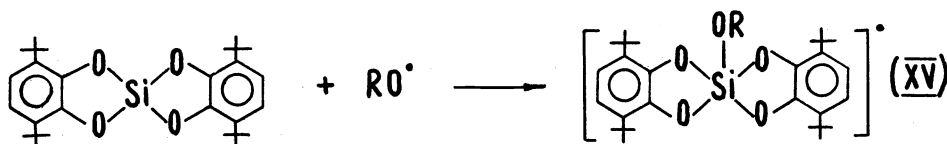
Aluminium derivatives show quite a similar behaviour. The spectrum of the organoaluminium radical (XIV) prepared as its boron analogue (Fig. 3)

<sup>\*)</sup> Intra- and interligand exchange effects are treated more rigorously below.

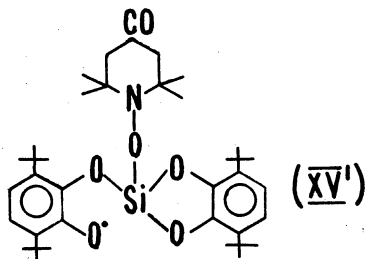


contains an aluminium sextiplet (nuclear spin of 5/2) split into a 1:2:1 triplet at  $-110^\circ$  and into a binomial quintiplet at  $0^\circ\text{C}$ . The exchange thus only involves one ligand at the lower temperature, whereas interligand exchange occurs at the higher temperature. The latter is responsible for high frequency valency wandering ( $\nu_{20} = 1.25 \cdot 10^{10} \text{ sec}^{-1}$ ). It thus appears that with boron and aluminium, the exchange cannot fully be quenched: intraligand exchange goes even at as low as  $-110^\circ\text{C}$  temperature. Four-well potential systems containing silicon show a different behaviour.

Free radicals containing formally five-coordinate silicon are formed from bis-3,6-di-tert.butylpyrocatechol silicon derivative under the action of stable radicals  $\text{RO}\cdot$  [14]:



This is a typical four-well potential system. By way of example, we shall describe the ESR spectrum of one of such radicals (XV'). At high temperature ( $+80^\circ\text{C}$ ), it contains a quintiplet with a binomial intensity ratio arising from the presence of four equivalent protons, 4, 4', 5, and 5'; at low temperatures ( $-110^\circ\text{C}$ ) it becomes a doublet of doublets corresponding to quenched structure XV'



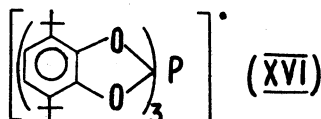
At  $-110^\circ$ : d. 1:1,  $a_{\text{H}(4)} = 6,37 \text{ oe}$ ;  
 d. 1:1,  $a_{\text{H}(5)} = 2,37 \text{ oe}$ ;  
 at  $+80^\circ$ : quint. 1:4:6:4:1,  
 $a_{\text{H}} = 2,18 \text{ oe}$ .

in which free valency is fixed at one of the oxygen atoms. The unpaired electron thus rapidly runs over four oxygen atoms of both pyrocatechol ligands at high temperatures and "adheres" to one of the oxygen atoms at low temperatures.

Under heating above  $100^\circ\text{C}$ , the exchange also involves the iminoxyl radical which undergoes elimination and shows a characteristic ESR hyperfine structure. The process is reverse to the reaction of the formation of radical (XV'). More examples of four-well potential systems will be given below. We now turn to six-well potential systems and to phosphorotropy.

### 3. SIX-WELL POTENTIAL SYSTEMS. PHOSPHOROTROPY.

Phosphorotropy was first studied by us for radical (XVI) containing a formally six-coordinate phosphorus atom.



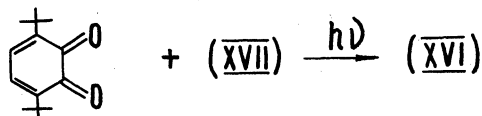
A number of reactions were applied to generate this radical [15].

1. Spirophosphorane (XVII) was made from 3,6-di-tert. butylpyrocatechol and phosphorus trichloride by analogy to the well known Anschütz synthesis [16]:

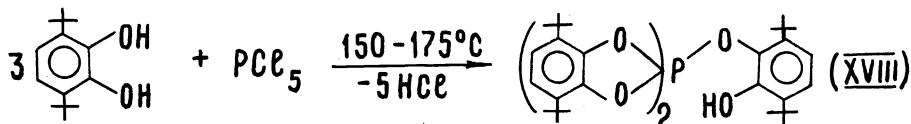


(M.p. 186-187° (from CH<sub>3</sub>OH+CCl<sub>4</sub>), NMR,  $\delta$  <sup>31</sup>P(CCl<sub>4</sub>): -26,07 ppm. J<sub>PH</sub>=890 Hz)

Photochemical reaction of the resulting spirophosphorane with 3,6-di-tert-butyl-orthoquinone yielded (XVI):

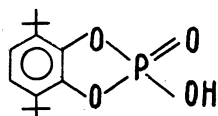


2. 2,6-Di-tert-butylpyrocatechol reacted with PCl<sub>5</sub> to give oxyspirophosphorane (XVIII):

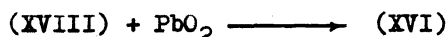


m.p. 208-209°; IR:  $\nu_{\text{OH}}$  2900 cm<sup>-1</sup>.

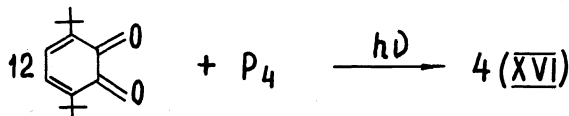
The product was unstable and decomposed slowly in the air to give phosphate:



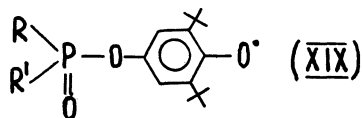
Oxidation of (XVIII) with lead dioxide gave radical (XVI) [17].



3. Lastly, the same free radical was obtained by photoaddition of 3,6-di-tert-butyl-orthoquinone to phosphorus element [17].



Solutions of free radical (XVI) obtained from different routes gave identical ESR spectra showing the same temperature dependence. The ESR spectrum of (XVI) in toluene is shown in Fig. 4. At 20°C, the spectrum consists of a phosphorus doublet with each component split into 7 lines of a 1:6:15:20:15:6:1 intensity ratio. The interpretation is unambiguous: the splittings are at phosphorus (4.0 oe) and six equivalent protons (1.45 oe). The unpaired electron thus interacts with all the six protons of three benzene rings and with phosphorus. The spin density at the phosphorus atom itself is not very high: the coupling constant of 4.0 oe is comparable to those observed in phenoxy radicals (XIX), 6 to 7 oe [18].



This drives one to the conclusion that unpaired electron spin density is mostly localized in the pyrocatechol fragments. Middle septiplet components broaden with temperature lowering, and the spectrum becomes a doublet of triplets at -80°C. The doublet splitting involves phosphorus and the trip-



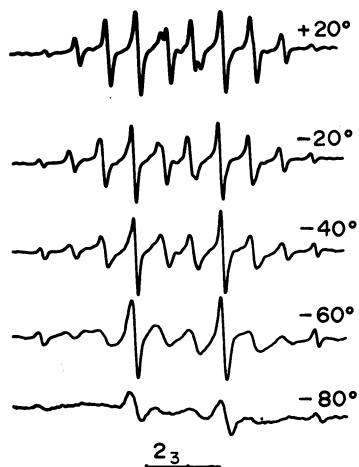
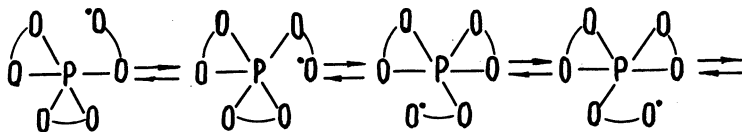


Fig. 4. ESR-spectrum of radical (XVI) in toluene. At +20°C: Doublet 1:1,  $a_p=4$  oe, septiplet 1:6:15:20:15:6:1,  $a_H=1.45$  oe. At -80°C: Doublet 1:1,  $a_p=4.0$  oe, triplet 1:2:1,  $a_H=4.35$  oe.

let splitting of 4.35 oe (i.e. three times as large as the septiplet splitting) is due to two protons of the same ring. Free valency thus wanders over all the six equivalent oxygen atoms at 20°C and higher temperatures

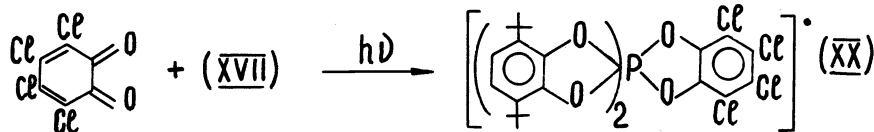


etc.

whereas ESR spectra obtained at lower temperatures are indicative of unpaired electron interactions with protons of one of the rings only.

Temperature dependence of the spectrum in ether was studied in more detail [17]. At low temperatures, the spectrum exhibits a quadruplet splitting (involving two protons and phosphorus, 1:3:3:1). Intermediate spectra are particularly well-defined and suitable for kinetic analysis. Temperature decrease proved to have near the same decelerating action on both intra- and interligand exchange. Nevertheless, under the conditions of quenching of interligand exchange, intraligand exchange occurring at approximately the same frequency is still observed (the spectral condition for fast exchange ( $\nu \gg \chi_g \cdot \Delta s$ ) remains fulfilled, with splitting at two protons). The corresponding kinetic parameter has the value of  $\nu_{20}=2,2 \cdot 10^9$  sec<sup>-1</sup>, i.e. the unpaired electron runs over all the six oxygen atoms with migration frequency of  $2 \cdot 10^9$  sec<sup>-1</sup> at 20°C.

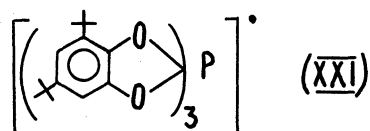
Spirophosphorane (XVII) reacts with orthochloroanil under irradiation to give free radical (XX) containing formally hexacoordinate phosphorus [15]:



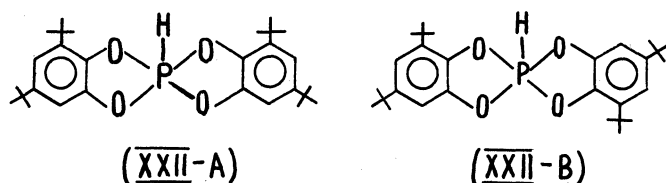
The presence of four chloro atoms in one of the rings suggests that spin density should mainly be distributed over two other pyrocatechol fragments and phosphorus atom. In fact, the ESR spectrum of the radical at -80°C is a 1:3:3:1 quadruplet (hyperfine splitting at phosphorus and two protons of the same ring). At higher temperatures (-40°C) the spectrum transforms

into a doublet of quintiplets (1:4:6:4:1) corresponding to four equivalent protons. Phosphorus splitting is equal to 4.35 oe, and splitting within the quintiplet has the value of 2.18 oe<sup>Ⓜ</sup>. It is noteworthy that the quintiplet splitting is 1.5 times larger than the septiplet splitting in asymmetrical radical (XVI) (1.45 oe). This implies that the same spin density is distributed over four and six protons in the former and the latter radicals, respectively. Hence it follows that all the spin density distributed over three ligands in (XVI) is localized in two ones in (XX) which thus is a four-well potential system. The perchlorinated ligand does not participate in delocalization of spin density.

Important results were obtained in the study of phosphorus-containing free radicals incorporating the asymmetrical ligand, the 3,5-di-tert.butylphenylene-1,2-dioxy group. The corresponding triligand radical (XXI) was also prepared by a number of reactions [19].

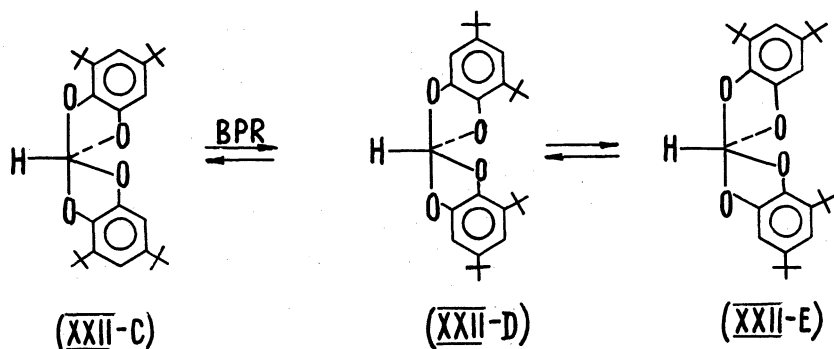


1. Starting from spiroposphorane (XXII) which is a mixture of isomers:



The starting compound was isolated from reaction of 3,5-di-tert.butylpyrocatechol with  $\text{PCl}_3$  in ether in a 50-55% yield. M.p. 188-190°C. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum of the compound contained two signals at  $\delta = -22.88$  and  $-23.36$  ppm,  $J_{\text{PH}}$  of 876.5 and 892.3 Hz.

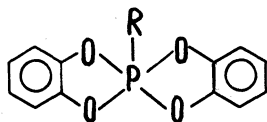
The compound having a square pyramidal configuration should contain two isomers (forms A and B) and, accordingly, give two NMR signals. In the case of trigonal bipyramidal geometry, three isomers should occur (C, D and E).



Isomers C and D are related to each other by low-barrier Berry pseudorotation. Provided the exchange  $\text{C} \rightleftharpoons \text{D}$  occurs at a high frequency, whereas interconversions  $\text{C} \rightleftharpoons \text{E}$  and  $\text{D} \rightleftharpoons \text{E}$  are low-frequency processes, which is quite a natural supposition, the  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum should contain two signals which agrees with the experimental data.

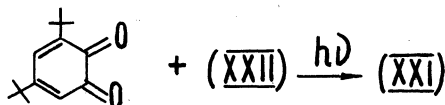
Spiroposphoranes of the type:

<sup>Ⓜ</sup> Radical (XX) is unstable and decomposes even at  $-40^\circ\text{C}$  which complicates the spectrum.

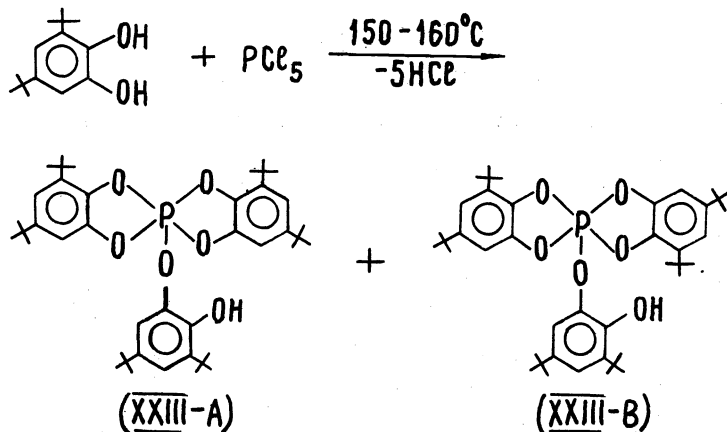


have been studied by X-ray diffraction. With Cl [20a], Ph [20b], CH<sub>3</sub> [20c] or OPh [20d] for R, the molecules have a near square pyramidal geometry in the solid state with only slight distortions in the direction of a trigonal bipyramid due to Berry pseudorotation. Calculations show that the distortion is the strongest with F for R. The square pyramidal geometry thus predominates in the crystal structures of spirophosphorenes of this type. If the same remains valid with the hydrogen derivative (R = H) and if the molecular structure does not change on going into the liquid phase, the occurrence of two isomers XXII-A and XXII-B is quite a natural suggestion. In the case of a strong trigonal distortion, the second explanation applies.

Photoreaction of spirophosphorene (XXII) with 3,5-di-tert.butyl-orthoquinone in toluene yields radical (XXI).



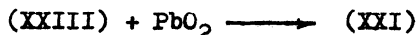
2. The second route to (XXI) is based on oxyspirophosphorene (XXIII) prepared from 3,5-di-tert.butylpyrocatechol and PCl<sub>5</sub> in the yield of about 40% at 150-160°C (also a mixture of isomers).



It melts within a rather wide temperature interval (118-141°C) and also shows duplicate <sup>31</sup>P-<sup>1</sup>H NMR signals, -27.6 and -28.11 ppm. The problem of isomerism of (XXIII) is similar to that of (XXII). In the present case, square pyramidal configuration is, however, the more probable one (cf. [20d]).

Bases act on spirophosphorene (XXIII) to give a hexa-coordinate phosphate anion. Thus, the <sup>31</sup>P-<sup>1</sup>H NMR spectrum of a mixture of (XXIII-A) and (XXIII-B) in pyridine contains one signal at  $\delta = -82.2$  ppm which is typical for a six-coordinate phosphorus of this type [21].

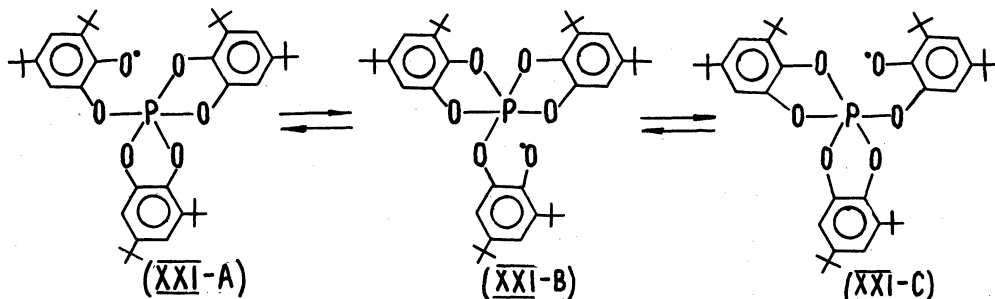
Spirophosphorene thus prepared is then subjected to oxidation in toluene with lead dioxide under vacuum or with tert.butylperoxide under UV irradiation.



3. The third route to (XXI) is a photoreaction of 3,5-di-tert.butyl-orthoquinone with phosphorus element [17] discussed below.

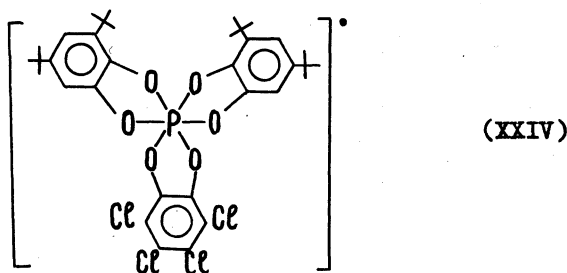
The ESR spectrum of (XXI) shows a strikingly interesting temperature dependence [19]. At a low temperature (-100°C), it is a 1:2:1 triplet. The hyperfine splitting at phosphorus is equal to that at the meta-hydrogen nucleus,  $a_P = a_H(5) = 4.35$  oe. The radical should be assigned the structure with

the unpaired electron localized, naturally, at the sterically hindered oxygen atom adjacent to the tert.butyl group and with phosphorus linked with a sterically nonhindered oxygen atom, i.e. A, B, or C:

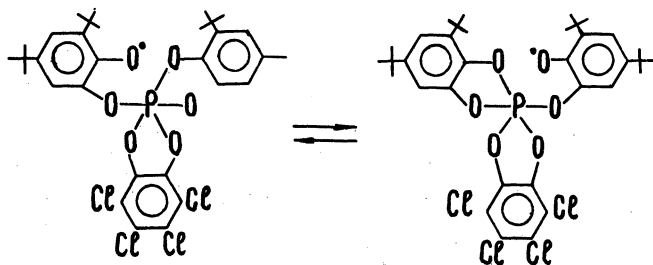


It would be pertinent to remind here that no hydroxyl hydrogen migration occurs in di-tert.butylphenoxy radical (VI) where free valency is localized at the sterically hindered oxygen atom. Additional broad lines appear in the ESR spectrum of (XXI) with temperature rise. These undergo gradual narrowing, and at  $-40^{\circ}\text{C}$ , the spectrum consists of a phosphorus doublet ( $a_p = 4.35$  oe) and a 1:3:3:1 quadruplet with splitting of 1.45 oe, i.e. just three times less than that observed at the low temperature. It thus follows that the splitting is due to three equivalent protons which may only be the 5, 5', and 5'' protons present in all the rings and positioned between the tert.butyl groups, para- to the oxygen atoms linked with phosphorus. The triligand system is thus a three-well potential one, the interligand exchange being the only exchange mechanism involved.

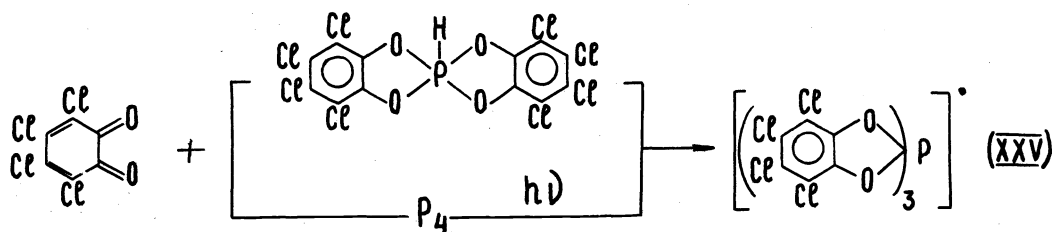
The synthetic technique described above was also applied to generate radical (XXIV):



At  $-100^{\circ}\text{C}$ , its ESR spectrum is a 1:2:1 triplet similar to that observed in radical (XXI) ( $a_p = a_H(5) = 4.35$  oe), and at  $-40^{\circ}\text{C}$ , it is a doublet of 1:2:1 triplets ( $a_p = 4.34$  oe,  $a_H(5) = 2.17$  oe). The ring proton splitting at  $-40^{\circ}\text{C}$  is thus half as large as at  $-100^{\circ}\text{C}$ . As the o-chloroanil ligand does not participate in the exchange and free valency may only migrate to a sterically hindered oxygen atom (more accurately, phosphorus may only attach to a sterically nonhindered one), the system is a two-well potential one with interligand exchange only.



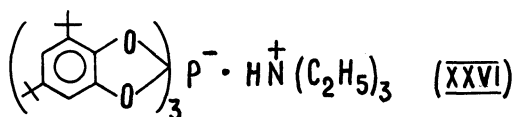
Perchlorinated radical (XXV) was isolated from two reactions [17]:



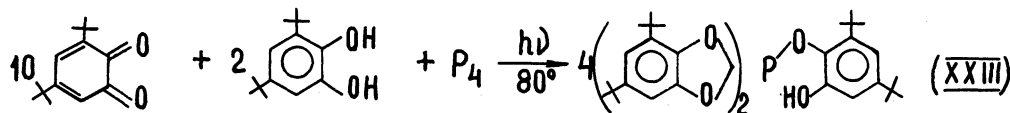
Its ESR spectrum only contains a phosphorus doublet ( $a_p=3.4$  oe). By analogy, radical XXV may be treated as six-well potential system, though this cannot be proved since splitting at chloro nuclei cannot be observed.

#### 4. REACTIONS OF ORTHO-QUINONES WITH PHOSPHORUS

The problem of photochemical reactions of orthoquinones with phosphorus element has been studied by us in detail using 3,5-di-tert.butylorthoquinone as quinone reagent. We have already mentioned, that radical (XXI) occurs in the reaction of this compound with white phosphorus in toluene under irradiation. If the process is carried out in the presence of triethylamine and under heating, crystalline six-coordinate phosphorate (XXVI) is formed in a small yield.

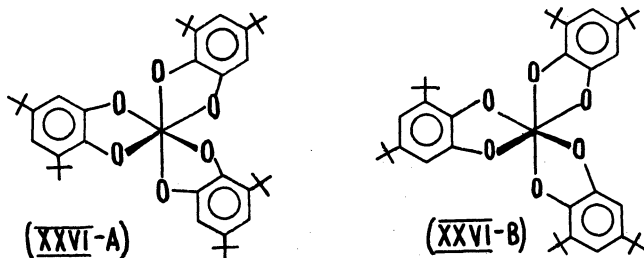


Its  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum in acetonitrile consists of two signals in the range  $-83$  to  $-84$  ppm. The formation of phosphorate (XXVI) from radical (XXI) implies one-electron reduction. In fact, two isomeric oxyphosphorane (XXIII) (A and B) are formed in the reaction:



in a high yield. The product was not isolated. It gives one of the isomers of phosphorate (XXVI),  $\delta^{31}\text{P}$ - $\{^1\text{H}\} = -83.69$  ppm (acetonitrile, 0.1 M,  $30^\circ\text{C}$ ), under the action of triethylamine in the absence of light. The second isomer with  $\delta^{31}\text{P}$ - $\{^1\text{H}\}$  of  $-83.73$  ppm (the same conditions) is formed in the reaction with triethylamine under irradiation at elevated temperatures. The isomers also differ by their m.p.'s. The yields of crystalline phosphorates in the two-step reactions are 68 and 66%, respectively.

Theoretically, two isomeric pairs of enantiomers may occur in phosphorate (XXVI).

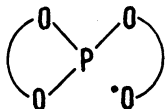


In one of the pairs, oxygen atoms on each of the octahedron axes have one meta- and the other one ortho- tert.butyl neighbour (form A). In the other pair of enantiomers, the tert. butyl substituents are positioned (i) ortho-, ortho-, (ii) meta-, meta-, and (iii) ortho-, meta- with respect to oxygen atoms on the same octahedron axis (form B). At present, we cannot assign  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR signals to definite forms.

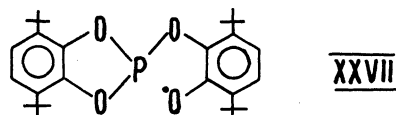
As evidenced by the  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectra of the 1- $\alpha$ -phenylethylamine salt, each of the forms is a racemic mixture. The isomers give two signals

-83.75 and each, at  $\delta$ -83.84 and -84.05 and -84.14 ppm, respectively (acetonitrile, the conditions are the same). Accordingly, a mixture of two isomers gives four signals, at  $\delta$  = -83.72; -83.83; -84.12; -84.19 ppm. Isomers A and B may be converted into each other via oxyspirophosphorane (XXIII). Oxidation of the latter, naturally, leads to free radical (XXI).

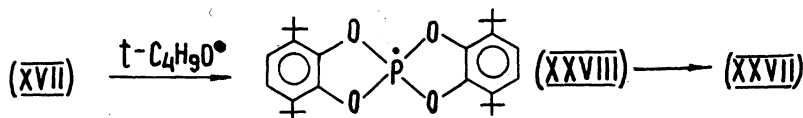
All these interconversions shed light on the photosynthesis of free radicals from ortho-quinones and phosphorus element. Ortho-quinones react as biradicals under photoexcitation and attack phosphorus tetrahedra causing homolytic cleavage of P-P bonds. The intermediate product should then be a free radical containing trivalent phosphorus:



which should readily add an excited ortho-quinone molecule. To verify this scheme, a solution of 3,6-di-tert.butyl-orthoquinone in toluene was irradiated in the presence of phosphorus at a low temperature ( $0 \sim -80^\circ\text{C}$ ). During irradiation, the ESR spectrum of radical (XXVII) [22]

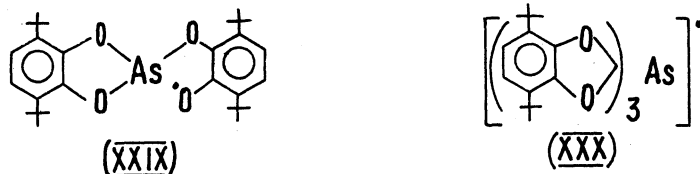


was registered together with the well known spectra of the ortho-oxyphenoxy radical (II) and radical (XVI). The former contained two doublets,  $a_{\text{P}}=58$  oe and  $a_{\text{H}}=13$  oe [22]. The same radical was generated from spirophosphorane (XVII) and di-tert.butyl peroxide. It is likely that the first-formed species is phosphoranyl radical (XXVIII).



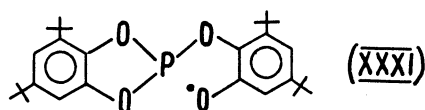
Phosphoranyl radicals of this type, are, however, not stable [23] and undergo  $\alpha$ -elimination to give radical (XXVII). The latter is unstable as well. It easily adds orthoquinone to produce a well known triligand radical (XVI). Similar results were obtained with 3,5-di-tert.butylorthoquinone. As the radicals mentioned only exist at low temperatures, we failed to observe the phenomenon of a wandering valency in this case.

Radical (XXVII) is unstable. Substitution of arsenic for phosphorus increases its stability considerably. Radical (XXIX) is generated by irradiation of yellow arsenic in solutions of 3,6-di-tert.butyl-orthoquinone [22].

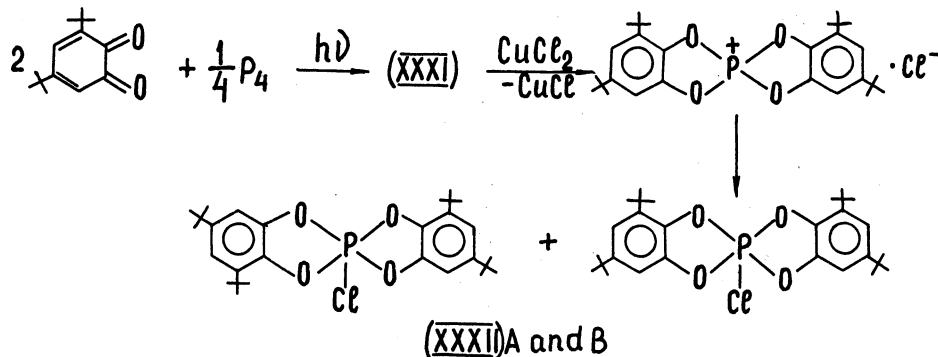


Its ESR spectrum shows temperature dependent behaviour, though splitting at arsenic nucleus remaining constant ( $a_{\text{As}}=19.5$  oe). The spectrum measured at temperatures above  $155^\circ\text{C}$  is indicative of free valency wandering over all the four oxygen atoms. At low temperatures, free valency is fixed at one of the oxygen atoms in one of the ligands ( $a_{\text{H}(4)}=7.65$ ,  $a_{\text{H}(5)}=0$ ). In the presence of excess orthoquinone, the addition of orthoquinone to radical (XXIX) occurs to give a triligand radical (XXX). In the latter, spin density on arsenic is rather small ( $a_{\text{As}}=0.4$  oe), whereas in (XXIX)  $a_{\text{As}}$  amounts to 19.5 oe. Antimony and bismuth form similar radicals [22].

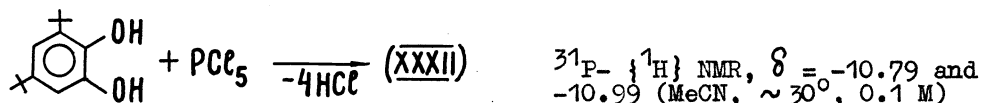
All those findings confirm our scheme of orthoquinone reaction with phosphorus. Lastly, the radical intermediate containing trivalent phosphorus may be oxidized to phosphonium cation. This was proved for radical (XXXI) generated from 3,5-di-tert.butylorthoquinone [22].



Irradiation of a mixture of 3,5-di-tert-butylorthoquinone and white phosphorus in benzene at 35°C in the presence of anhydrous CuCl<sub>2</sub> leads to precipitation of CuCl and formation of chlorophosphorane (XXXII) which is undoubtedly formed from the corresponding phosphonium cation.



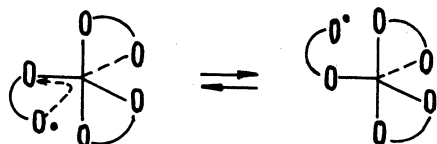
Crystals of (XXXII) (from hexane) melt in a wide temperature range (175-185°C). The product was identified by comparison with chlorophosphorane made from 3,5-di-tert-butylpyrocatechol and PCl<sub>5</sub> whose identity cannot be doubted (cf. [26]).



### 5. WANDERING VALENCY AND PSEUDOROTATION

It has already been noted that inter- and intraligand exchange in a six-well potential system containing three bidentate ligands such as free radical (XVI) have near the same frequency. Temperature lowering leads first to disappearance of spectral manifestations of interligand exchange while intraligand exchange is still observed because the condition for fast exchange,  $\nu \gg \delta_e \Delta a$ , is retained ( $\Delta a$ , the difference between the hyperfine splitting constants, is very small). It seems reasonable to assume that the instantaneous structure of free radical (XVI) and like species has a square pyramidal or trigonal bipyramidal geometry, and an intrinsic mechanism of free valency and bond shifts is S<sub>H</sub>2 or rather, its intramolecular version in the present case. The equality of inter- and intraligand exchange frequencies may be explained from one of the two basic principles discussed below.

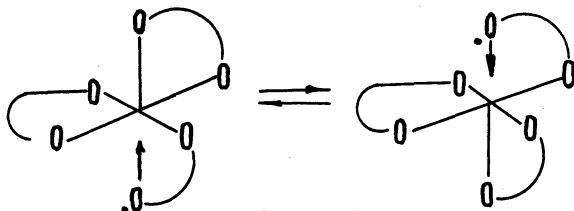
a) Nonlinearity of the transition state of the S<sub>H</sub>2 reaction, e.g. for an idealized trigonal bipyramid:



It is then easy to accept that free valency may wander over all the six vertices of an averaged octahedron with the same probability.

b) Linearity of the transition state during pseudorotation. The stereochemistry of the S<sub>H</sub>2 substitution in five-coordinate species has not been studied thus far. One may suggest that a linear transition state will be energetically favoured [23]. This should lead to interligand exchange only, e.g.

for a square pyramid:



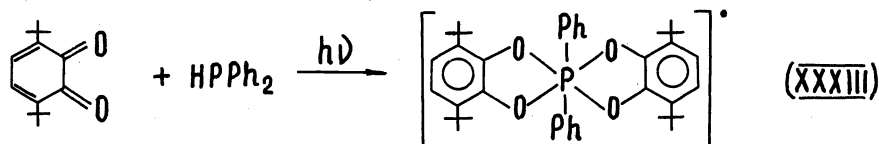
If fast pseudorotation contributes and if its frequency exceeds the  $S_{H2}$  exchange frequency, inter- and intraligand exchange frequencies converge. With a trigonal bipyramidal structure, the  $S_{H2}$  attack takes place during pseudorotation when the radical goes through a square pyramidal configuration and the free radical attacks the pyramid on the side of its base.

Pseudorotation frequencies known to occur in phosphoranes do not exceed  $10^5 \text{sec}^{-1}$  which is the upper limit of NMR detectable frequencies. The highest frequencies are observed in symmetrical oxyphosphoranes containing highly electronegative substituents [24]. Frequencies as high as  $10^6$  to  $10^9 \text{sec}^{-1}$  corresponding to ESR time scale were observed in the present work. With a lifetime of about  $10^{-6}$  to  $10^{-9}$  sec, a particle may survive thousands of vibrational motions, including pseudorotation motions. The ESR technique thus provides a means for studying higher frequency pseudorotations than can be studied by the NMR method.

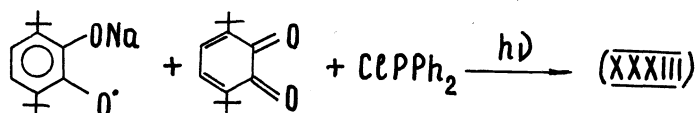
The intraradical  $S_{H2}$  reaction in radical (XVI) should involve an octahedral transition state. The high exchange rate makes all the six octahedron vertices equivalent. It thus follows that on the ESR time scale, radical (XVI) has an octahedral structure, although its instantaneous geometry is a square pyramid or trigonal bipyramid\*.

If all that has been said above gives an adequate description of the actual situation, pseudorotation frequency lowering below the  $S_{H2}$  reaction frequency should block intraligand exchange, without hindering interligand exchange. Accordingly, the number of potential surface wells in radical (XVI) and like systems should decrease.

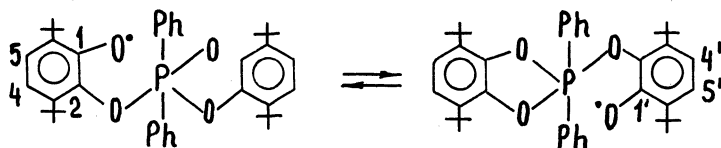
Pseudorotation frequency lowering may, e.g. result from the introduction of phenyl substituents at the phosphorane phosphorus atom. We have synthesized free radical (XXXIII) from 3,6-di-tert.butyl-orthoquinone and diphenylphosphine:



One more route to this radical elucidating its structure is as follows:



In the absence of pseudorotation, interligand exchange is only possible in this radical:

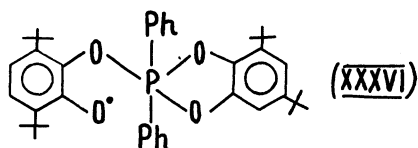
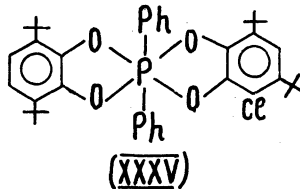
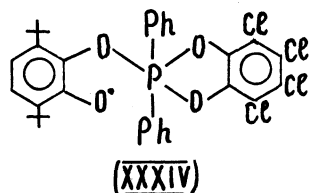


The ESR spectrum of the radical measured at  $+20^\circ\text{C}$  actually contains two triplets in addition to the phosphorus doublet ( $a_P = 0.56 \text{ oe}$ ). One of these

\*The fact that the octahedral structure is a transition state rather than an intermediate with free valency localized on phosphorus follows from smallness of hyperfine splitting on phosphorus ( $a_P = 4$  to  $4.5 \text{ oe}$ ).

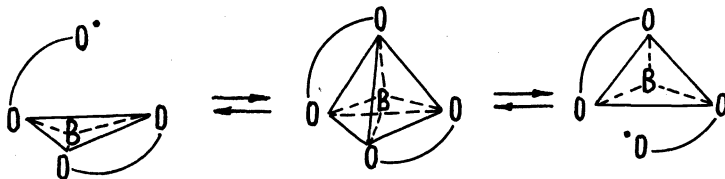


arises from equivalent protons 4 and 4' ( $a_H=2.95$  oe) and the other one from equivalent protons 5 and 5' ( $a_H=0.95$  oe). Free valency thus only shifts between the positions 1 and 4'. The system is a two-well potential one with interligand exchange. At  $-100^\circ\text{C}$ , the exchange is quenched and, together with the phosphorus doublet mentioned, the spectrum contains a doublet of doublets ( $a_H(4)=5.9$  oe,  $a_H(5)=1.9$  oe). All the spin density is localized in one of the ligands. It is pertinent to remind here of free radical (XX) which contains the ortho-chloroanil residue instead of two phenyl groups. This residue does not hinder pseudorotation. As a consequence, radical (XX) is a four-well potential system involving both intra- and interligand exchange. Lastly, radicals (XXXIV), (XXXV), and (XXXVI)



do not show ESR features characteristic of exchange at all. Low rate of pseudorotation compared with the  $S_{1/2}$  attack frequency hinders intraligand exchange in those radicals while the nature of the second ligand prevents interligand exchange.

Lastly, some points should be mentioned in connection with two-ligand four-well potential systems, such as pyrocatechol derivatives of boron (XIII) and aluminium (XIV). Again, inter- and intraligand exchange appears to occur at near the same frequency in those systems. The transition state may have a tetrahedral structure, while instantaneous structures should have a triangular geometry, with boron or aluminium in the centrum. Free valency "hangs" over the central atom.



Transition state

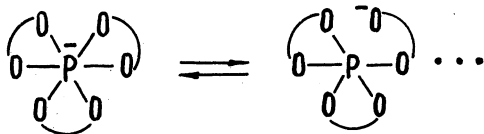
Its attack cleaves one of the equivalent B-O or Al-O bonds. Boron and aluminium atoms thus as if oscillate within the tetrahedron which results in tetrahedral symmetry of the radicals on the ESR time scale. The transition state is either nonlinear or corresponds to a local energy minimum with the unpaired electron on boron or aluminium. Small values of hyperfine splittings, however, provide an evidence against the latter suggestion ( $a_B=2.5$  oe,  $a_{Al}=2.58$  oe).

It thus follows that here again, free valency wandering increases the coordination number of the central atom by unity. This is, of course, the case of the observation time corresponds to the characteristic ESR time interval ( $10^{-7} > \tau > 10^{-10}$  sec).

We believe that free valency wandering is a very general phenomenon which should also play an important role in many other cases. The condition for its manifestation is that the wandering frequency be higher than inverse radical lifetime. We observed this phenomenon for kinetically stable free radicals characterized by large half-times. Such radicals, however, make up but a small portion of free radicals, much more numerous are free radicals with short but sufficient for "wandering" lifetimes.

It seems likely that enediol semidiones, species of great importance for biological systems, must display free valency wandering. It is also probable that such processes play an important role in redox transformations of sugars including their biochemical redox transformations.

Charge "wandering" may also occur in solutions of phosphate anions of the type:



Quite recently, French authors [25] have reported on easy interconversions of enantiomeric anions of this type. It is possible that the explanation lies in charge wandering over octahedron vertices. Like any novel phenomenon, free valency wandering stirs imagination and, therefore, stimulates experimental work.

To conclude, let me name the authors whose results have been described in the present lecture. These are A.I. Prokof'ev, N.N. Bubnov, S.P. Solodovnikov, V.V. Ershov, I.S. Belostotskaia, N.A. Malysheva, A.A. Khodak, D.I. Lobanov, M.I. Kabachnik et al.

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