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Stereochemistry of the Reactions of Phosphorus-containing Free Radicals

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The stereochemical characteristics of phosphoranyl radicals and β-phosphorus-substituted radicals as well as tautomeric transformations involving phosphorus-containing phenoxy-radicals, which reflect the stereochemical properties of quinquevalent phosphorus, are discussed.
The bibliography includes 58 references.

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I. INTRODUCTION

Phosphorus-containing free radicals and reactions involving them have been vigorously investigated in recent years. The results of experimental and theoretical studies on the structures and reactivities of numerous phosphorus-radicals published until 1974 have been compiled in two reviews[1,2]†.

In the study of the structures and reactivities of phosphorus-containing free radicals a research field associated with the stereochemistry of the radical reactions of organophosphorus compounds has been established. Ideas have been put forward, according to which the stereochemical transformations occuring in organophosphorus free radicals influence the mode and rate of reaction and also the stereochemical properties of the reaction products.

II. STEREOCHEMICAL CHARACTERISTICS OF PHOSPHORUS-CONTAINING FREE RADICALS

According to the established classification, phosphorus-centred free radicals are divided into phosphinyl, phosphonyl, and phosphoranyl radicals. In these radicals the unpaired electron is either wholly or largely localised at the phosphorus atom. There exists a large class of radicals in which the free valence is located at atoms in the β-positions relative to the phosphorus atom. The radical-anions and radical-cations of organophosphorus compounds are widely known[1,2].

A planar structure with the localisation of the unpaired electron in the *p* orbital of the phosphorus atom has been attributed to the phosphinyl radicals $\dot{P}R_2$.[1] It is believed that

† After the present review had been sent to the printers, the monograph by Ya.A.Levin and E.I.Vorkunova, "Gomoliticheskaya Khimiya Fosfora" (The Homolytic Chemistry of Phosphorus), Izd.Nauka, Moscow, 1978, was published; here the reader will find a more detailed discussion of a number of the problems dealt with in the present review.

the phosphonyl radicals $R_2\dot{P}O$ have a non-planar structure and the unpaired electron is in the 3*s* and 3*p* phosphorus orbitals and the 2*p* oxygen orbital[1]. The greatest amount of data are available on the structures of phosphoranyl radicals of the type $\dot{P}R_4$. Depending on the nature of the substituents, either a trigonal bipyramid (TBP) or a tetrahedral structure is attributed to them.

The non-equivalence of the fluorine atoms in the $\dot{P}F_4$ radical[3,4] or the hydrogen atoms in the $\dot{P}H$ radical[5] and the hydrogen atoms in the methyl groups in the $H_3\dot{P}O$–t-Bu, $Me\dot{P}H_2$–O–t-Bu, and $Me_3\dot{P}O$–t-Bu radicals[6], which follows from the EPR spectra, shows that the radicals have a structure close to that of a TBP, which is characteristic of phosphorus(V) compounds.

The following stereochemical problems arise in the study of phosphoranyl radicals[7].

(a) Is the formation of a phosphoranyl radical following the addition of an attacking radical (for example in the apical position, as in the nucleophilic attack on PX_4^+, $X_3P=O$, and possibly $:PX_3$) stereoselective?

(b) Is there a possibility of the interconversion of the configurational isomers during the lifetime of the radicals, which naturally can vary as a function of the experimental conditions?

(c) Is the fragmentation of phosphoranyl radicals stereoselective, particularly when the phosphoranyl radical contains a pair of identical ligands, one of which is in the apical position and the other in the equatorial position and which one of them is susceptible to more or less ready α- or β-cleavage?

$$A{-}B^{\cdot} + PX_3 \rightarrow AB{-}\dot{P}X_3 ,$$

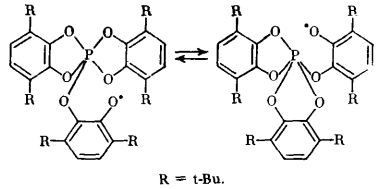
$$AB\dot{P}X_3{-}\left|\begin{array}{l}\xrightarrow[\alpha\text{-elimination}]{} A{-}B{-}PX_3 + X^{\cdot} ,\\ \xrightarrow[\beta\text{-elimination}]{} A^{\cdot} + B{=}PX_3 .\end{array}\right.$$

(d) The question arises which isomer of the phosphoranyl radicals recorded or not recorded by EPR undergoes faster fragmentation and which is the main source of the fragmentation products:

(e) Finally it is necessary to establish to what extent the stereochemical characteristics of the disposition of the substituents and the frequency of the interconversions of the stereoisomers of phosphoranyl compounds differ compared with phosphorus(V) compounds.

In the study of radicals where the free valence is localised on atoms in the β-positions relative to the phosphorus atom stereochemical problems associated with the steric requirements of the radical fragments also arise.

Exchange reactions involving radicals of the following type have been discovered recently:



R = t-Bu.

(I)

where the rapid transfer of the unpaired electron between the ligands results in the phosphorus(V) compound having the structure of a hexacoordinate phosphorus compound on the EPR time scale[8]. The study of this reaction led to the problem of the stereospecificity of the substitution reaction involving bonds and radicals with the TBP structure.

The main aspects of the stereochemical problem under consideration is the possibility of the interconversion of the configurational isomers of the radicals, their frequency and activation barriers, the mechanisms of stereochemical transformations, and their role in the overall mechanism of the radical reactions of organophosphorus compounds. The study of the stereochemistry of phosphoranyl radicals is based on the findings obtained in the study of phosphorus(V) compounds with which the radicals have much in common according to experimental data.

X-Ray diffraction and NMR data established that the geometry of these compounds corresponds to either a TBP or a tetragonal pyramid (TP). In agreement with calculations, the energy differences between these conformations are small (~0.5 kcal mol^{-1}). It has come to be assumed that in the liquid phase the majority of phosphorus(V) compounds have the TBP geometry[9].

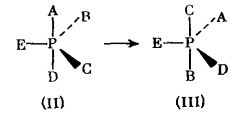
The so-called polarity rule has been established[9,10], according to which electron-donating substituents occupy equatorial positions in TBP, while electronegative substituents occupy apical positions (the vacant *d* orbitals of the phosphorus atom interact effectively with electron-donating substituents via the formation of dative bonds in the equatorial positions). Apart from the donor–acceptor interactions, steric effects play a major role, the apical position being more shielded. All these features make the apical bonds longer than the equatorial bonds.

It has been noted that for cyclic ligands, particularly oxygen-containing cyclic ligands, five-membered rings occupy preferentially the equatorial-apical positions because the internal strain is reduced in this configuration. Six-membered rings are located mainly in the equatorial positions[10]. The presence of identical ligands leads to additional stabilisation as a result of the ligand symmetry. It consists in the fact that isomers having identical ligands in either apical or equatorial positions are more stable.

Thus the disposition of the substituents in phosphorus(V) compounds is a complex function of several parameters. The concept of "apicophilicity" of particular ligands, based on empirical data, is used to describe this function[9,10].

The use of NMR made it possible to follow, in an enormous number of examples, the dynamics of the mutual exchange of ligands in a TBP, in which the substituents exchange between the apical and equatorial positions. It was found that the frequencies of such transformations depend significantly on the nature of the ligands and the activation energy varies within wide limits (1.5–25 kcal $mole^{-1}$).[9]

The ligand exchange in the chiral phosphorane



(II) (III)

can be explained within the framework of two models: (1) Berry's pseudorotation mechanism[11], taking into account the change in the angles in the TBP, which leads to a TP as an intermediate conformation with formation of a new TBP, and (2) the Ramirez turnstile mechanism[10], which postulates the rotation of three ligands relative to two others and reflects the transposition mechanism of the pseudorotation. The turnstile mechanism is more applicable to the explanation of ligand exchange involving cyclic phosphorus compounds, where Berry's pseudorotation is accompanied by an increase of ring strain when the angles are altered.

Five different types of rearrangements of the TBP of the phosphorane P(ABCDE), denoted by *M*1–*M*5, are distinguished[12]. The rates of different rearrangements and the stability of the conformers depend on the nature of the ligands. In the stereochemistry of nucleophilic substitution at a tetracoordinate phosphorus atom the formation of an

intermediate (or transition state) with a pentacoordinate phosphorus atom, having the TBP geometry, is postulated. The empirical rule that the attacking nucleophile enters the apical position and the substituted ligand leaves the apical position has been established and has been widely confirmed on numerous examples[10]. Hexacoordinate phosphorus species are anions and have the octahedral configuration.

III. STEREOCHEMICAL TRANSFORMATIONS OF PHOSPHORANYL RADICALS

A TBP structure with the free valence located in the equatorial plane has been attributed to phosphoranyl radicals:

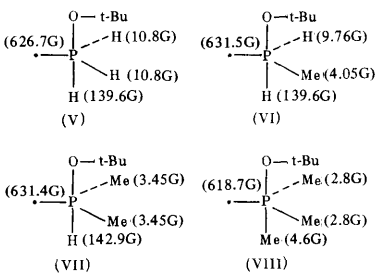


(IV)

This geometry has been established on the basis of the study of EPR spectra and theoretical analysis.

The EPR spectra of the simplest phosphoranyl radicals $\dot{P}F_4$ and $\dot{P}H_4$ show a non-equivalent hyperfine interaction (HFI) of the unpaired electron with the fluorine and hydrogen nuclei. In $\dot{P}F_4$ two fluorine atoms have an HFI constant of 259 G, while two others have a constant of 59 G; in $\dot{P}H_4$ two hydrogen atoms have an HFI constant of 198 G and two others have a constant of 6 G. The high HF constants involving the phosphorus atom (a_P), which amount to 1330 G in $\dot{P}F_4$ and 519.3 G in $\dot{P}H_4$, are associated with the appreciable *s* character of the hybrid *spd* orbital of the unpaired electron. Theoretical analysis[13,14] made it possible to assign the higher values of a_F and a_H to the apical positions and the lower values to the equatorial positions.

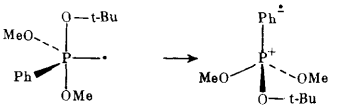
The EPR spectra of $\dot{P}F_4$ and $\dot{P}H_4$ were obtained in solid matrices. However, numerous examples of phosphoranyl radicals with a marked non-equivalence of the apical and equatorial substituents have also been obtained in solution. A number of phosphoranyl radicals in solutions in hydrocarbons have been obtained[6] at a low temperature by the addition of the t-butoxy-radical to the phosphines PH_3, CH_3PH_2, $(CH_3)_2PH$, and $(CH_3)_3P$. The structure of the radicals is shown in the diagram below, the values of the HFI constants being indicated opposite the corresponding atoms:



Thus the structure of phosphoranyl radicals is similar to that of phosphorus(V) compounds (phosphoranes), where the orbital of the unpaired electron acts as one of the substituents. It is therefore of great interest to follow the stereochemistry of the disposition of the substituents in phosphoranyl radicals and to compare it with the stereochemistry of the corresponding phosphoranes.

Roberts and coworkers carried out extensive studies in this field. They established that the chlorine atoms in chlorophosphoranyl radicals occupy apical positions preferentially. The EPR spectra of phosphoranyl radicals of the type t-Bu–O–$(RO)_n\dot{P}Cl_{3-n}$ and t-Bu–O–$R_n\dot{P}Cl_{3-n}$ have been investigated and show electron–Cl HF constants of 30–40 G.[15] In the EPR spectrum of $\dot{P}Cl_4$ the splitting by the apical chlorine atoms is 62 G and that by the equatorial atoms is 7 G.[16]

In the study of phenyl-substituted phosphoranyl radicals the fundamental problem of their structure arose (a TBP or tetrahedral structure). Doubts about the TBP structure of phenyl-substituted phosphoranyl radicals arose in view of the extremely low phosphorus hyperfine interaction constants in the corresponding radicals. Thus $a_P = 9.7$ G for t-Bu–O(Ph)$\dot{P}$·(OMe)$_2$ and we have $a_H^{para} = 9.7$ G, $a_H^{ortho} = 5.5$ G, and $a_H^{meta} = 0.9$ G.[17,18] On the basis of these data, it was suggested that the structure of phenyl-substituted phosphoranyl radicals changes from a TBP to a tetrahedron and that the radical itself acquires the betaine structure:



(IX) (X)

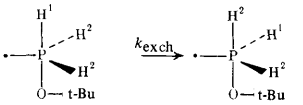
Numerous examples of radicals of this type have been presented in reviews[1,2].

Analysis of the hyperfine structure of the EPR spectra of a large number of phosphoranyl radicals established the apicophilicity series for substituents at the phosphorus atom[19,20]:

$$F, Cl, RC(O)O > CF_3, \overline{CH_2CH_2CH_2C(O)N}, OCN > RO, R_2N > H > H_3C.$$

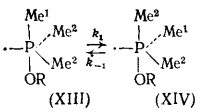
This apicophilicity series agrees on the whole with the electronegativities of the substituents and is consistent with the general characteristics established in the study of phosphorus(V) compounds. The study of the EPR spectra of phosphoranyl radicals over a wide temperature range showed that, with increase of temperature, an interchange of the ligand positions at a frequency of 10^6–10^8 s^{-1} is observed in some cases.

Krusic and Meakin[21] measured the frequency of exchange between two types of hydrogen atoms in t-BuO$\dot{P}H_3$ and the corresponding activation barrier and found that $\Delta G^{\neq} = 5.3$ kcal mole^{-1} at −75 °C and $k_{exch} = 3 \times 10^6$ s^{-1} at −80 °C:



(XI) (XII)

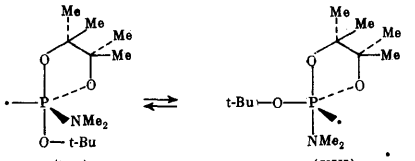
A similar example is provided by the t-butoxytrimethylphosphoranyl radical, in which the methyl groups change positions[22]:



(XIII) (XIV)

$k_1 = 4 \times 10^6$ s^{-1} at −70 °C. The temperature dependence of the rate constant is of the form $\lg k_1 = (10.4 \pm 1) - (13 \pm 4)$ kcal mole^{-1} θ^{-1}, where $\theta = 2.3\,RT$ kcal mole^{-1}. The rate of ligand exchange involving methyl groups is independent of the nature of the alkoxy-group (R = Et, t-Bu, or t-pentyl). It has been stated that[18] in certain trimethyl (R,R') phosphoranes similar methyl exchange frequencies are observed.

Another example where the ligands change positions is provided by the aminophosphoranyl radical[23]:



(XV) (XVI)

In contrast to the previous case, the states of the radicals (XV) and (XVI) are energetically different. The spectroscopic characteristics of the radicals (XV) and (XVI) differ appreciably:

Radical	(XV)	(XVI)
a_P, G	849	784
a_N, G	8.4	24

At −120 °C the ratio of the radical concentrations is (XVI)/(XV) = 0.25. With increase of temperature, the rate of interconversion of radicals (XV) and (XVI) increases, which is manifested by a characteristic broadening of the hyperfine structure (HFS) components associated with the nitrogen nuclei. Agreement between the experimental and calculated spectrum was achieved for $k_1 = 2.0 \times 10^7$ s^{-1}, $k_{-1} = 8.0 \times 10^7$ s^{-1}, and (XVI)/(XV) = 0.25 at −120 °C and $k_1 = 10^8$ s^{-1}, $k_{-1} = 3.3 \times 10^9$ s^{-1}, and (XVI)/(XV) = 0.3 at −80 °C.[23]

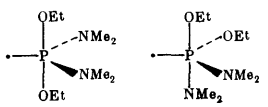
The following equation holds in the range between −120 °C and −80 °C:

$$\lg k_1 = 10.7 - 2.4/\theta,$$

where $\theta = 2.3\,RT$.

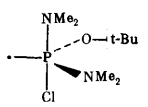
The temperature dependence of the equilibrium constant K = (XVI)/(XV) in the range from −160° to −120 °C makes it possible to determine $\Delta H^\circ \cong \Delta G^\circ \cong 0.4$ kcal mol^{-1} and $\Delta S^\circ \cong 0$.

The interaction of EtO· with $EtOP(NMe_2)_2$ gives rise to two radicals, namely (XVII) and (XVIII):



(XVII) (XVIII)

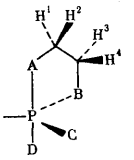
At −126 °C the concentration ratio [XVIII]/[XVII] = 6. At −140 °C each component of the phosphorus doublet in the spectrum of radical (XVIII) is split into a 1 : 1 : 1 triplet ($a_N = 11.5$ G). With increase of temperature to −110 °C, the three lines are replaced by five lines with a splitting of 7.5 G, and at −90 °C their intensity ratios become close to 1 : 2 : 3 : 2 : 1. These changes are attributed to the rapid exchange between the NME_2 groups in the apical and equatorial positions in the radical (XVIII) ($k_{exch} = 10^8$ s^{-1} at −110 °C).[23] In the radical[24]



(XIX)

the exchange of the dimethylamino-groups takes place at a rate of 2×10^7 s^{-1}, i.e. is somewhat slower than in the radical $(EtO)_2\dot{P}(NMe_2)_2$.

In the EPR spectra of the radicals of 1,3,2-dioxaphospholane and 1,3,2-diazaphospholane derivatives[23,24]

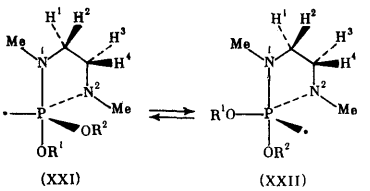


(XX)

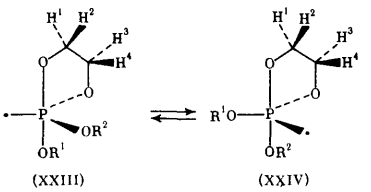
where A = B = O or A = B = N–Me, a hyperfine splitting by the quasi-apical ring protons H^1 or H^2 is observed and can serve as a source of information about the stereochemical mobility of these radicals.

For the above radicals, different stereochemical reactions are possible:

Exocyclic process 4*M*

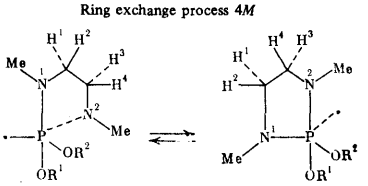


(XXI) (XXII) (1)

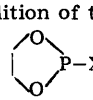


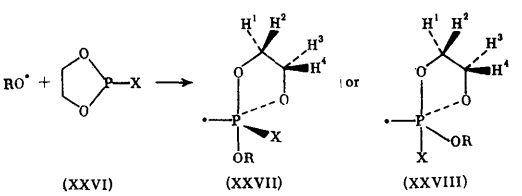
(XXIII) (XXIV) (2)

Ring exchange process 4*M*



(XXI) (XXV)

The addition of the alkoxy-radical RO· to 1,3,2-dioxaphospholane  as well as 1,3,2-diazaphospholane can proceed stereospecifically depending on the electronegativity of X:

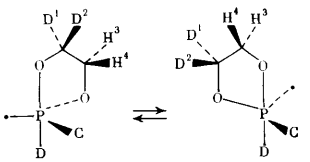


(XXVI) (XXVII) (XXVIII)

At a low temperature hyperfine splitting by one H^1 or H^2 proton is observed in the spectra of radicals formed from 1,3,2-dioxaphospholane when RO and X have markedly different apicophilic properties; the hyperfine interactions with the H^1 and H^2 protons are different owing to the differences between the steric orientations of these protons relative to the unpaired electron. When X and RO are identical, hyperfine splitting by the two equivalent protons ($a_H = 2$ G), caused by by the rapid exchange via reaction (2), is observed.

For C = D = OEt, the exocyclic process 4*M* takes place with $k_{exch} > 6 \times 10^9$ s^{-1} over the entire experimental temperature range. When C = OEt, D = Cl, and Cl is much more apicophilic than OEt, the groups change positions in the ring. The same process is observed for D = $MeCO_2$, CF_3CO_2, BzO, and $(EtO)_2P(O)O$. On the other hand, if D = F, OCN, and $CH_2(CH_2)_2C(O)N$, changes in line form are not observed, which indicates the absence of ligand position interchange[23,24].

The exocyclic 4*M* process and the exchange process in the ring were resolved using 4,4-dideutero-1,3,2-dioxaphospholanes. The resolution was achieved on the basis of the different HFS changes in spectra of the protonated and 4,4-dideutero-derivatives of the radicals when the temperature is varied:

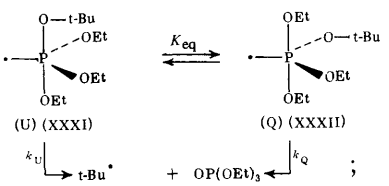


(XXIX) (XXX)

In the interchange of positions in the rings of radicals of 4,4-dideutero-derivatives of 1,3,2-dioxaphospholanes, the spectra are altered; with increase of temperature, there is a transition from the superposition of the doublet due to one proton in one pseudoapical CH_2 group (with a splitting of 4 G) on to a singlet due to one pseudoapical CD_2 group to a doublet with a splitting of 2 G, which corresponds to rapid migrations of the CH_2 and CD_2 groups between the apical and equatorial positions. In the exocyclic 4*M* process involving the protonated form there should be a change from a doublet with a splitting of 4 G to a 1:2:1 triplet with a splitting of 2 G. For the deutero-derivative at a high temperature, a singlet due to the deutero-group should be superimposed on the triplet and the resultant spectrum should have intensity ratios of 1:6:1, which has been observed experimentally[24].

The results show that the ligand positions are interchanged in the phosphoranyl radicals; the rate and nature of these processes are determined by the structural characteristics of the radicals.

The study of ligand exchange processes in phosphoranyl radicals involves the investigation of the chemical reactions of these radicals. Thus the mobility of the leaving group in the apical and equatorial positions is very important for the β-elimination reaction. The equilibrium between the stereoisomers can influence the observed β-elimination rate constant in the following way:



(U) (XXXI) (Q) (XXXII)

$$k_{obs} = (k_U + k_Q K_{eq})/(1 + K_{eq}).$$

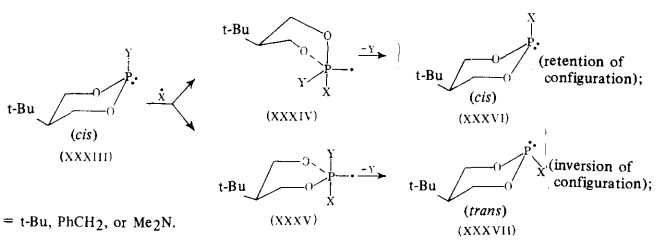
Thus in the elimination of the t-butyl radical with equilibrium between the stereoisomers, cleaved at different rates, will influence significantly the rate of the chemical reaction.

Kinetic studies have revealed definite stereochemical relations for α- and β-elimination reactions involving phosphoranyl radicals[22,25-28]. It has been suggested that in tetraalkoxyphosphoranyl radicals β-elimination takes place preferentially in the equatorial position, while α-elimination in alkoxyalkylphosphoranyl radicals takes place from the apical position[22,25].

A definite relation has been observed between the stability of phosphoranyl radicals and the change in the number of alkyl and alkoxy-groups in the radical[27]. The maximum stability is observed when the numbers of alkyl and alkoxy-groups are equal. This is attributed to the fact that, in conformity with their more pronounced apicophilic properties, the alkoxy-groups are located in the apical positions, while the alkyl groups are in the equatorial positions[27]. Thus the groups involved in α- and β-elimination are located in chemically inactive positions.

Stereochemical transformations are important in homolytic substitution reactions involving phosphorus(III) compounds. Bentrude and coworkers[29,30] studied the stereochemistry of radical substitution and oxidation of phosphorus(III) compounds[29,30] In the course of the investigation of these reactions the problem arose of the configurational stability of the phosphoranyl radicals formed and of its influence on the yield of the isomers.

The stereochemistry of the substitution reaction was studied in the following example[29];



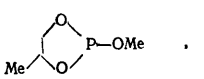
(cis) (XXXIII) (XXXIV) (XXXV) (cis) (XXXVI) (trans) (XXXVII)

(retention of configuration); (inversion of configuration);

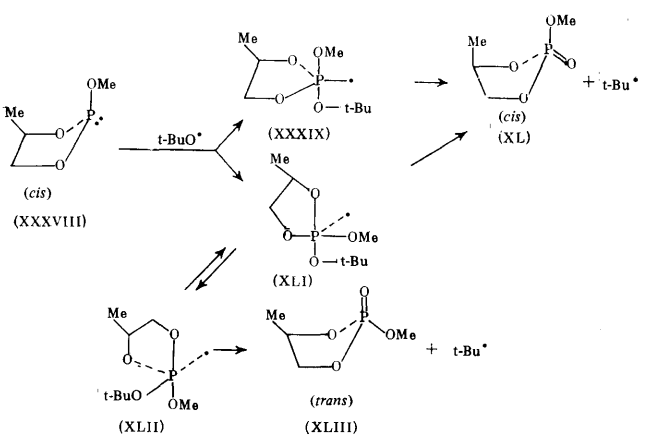
Y = t-Bu, $PhCH_2$, or Me_2N.

The radical X· was Me_2N·, obtained in the decomposition of the tetrazene $Me_2NN{=}NNMe_2$ under the influence of ultraviolet light. These reactions proceed with a high degree of stereoselectivity and lead mainly to inversion of configuration. It has been suggested that the disposition of X and Y in the apical positions in structure (XXXV) is responsible for the observed inversion of configuration.

The stereochemistry of the oxidation reactions of phosphorus(III) compounds has been studied[30] for the compound

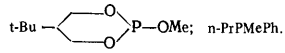


It was found that the reaction is stereospecific and proceeds with retention of configuration. The retention of configuration implies that the β-decomposition of phosphoranyl radicals is faster than the ligand exchange (XLI) → (XLII):



(cis) (XXXVIII) (XXXIX) (cis) (XL) (XLI) (XLII) (trans) (XLIII)

The retention of configuration was observed previously[31] in the study of the oxidation of the following compound:

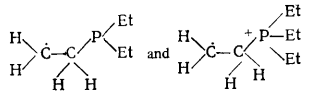


The stereospecificity of the above reactions implies a "memory" of the pathways followed in the formation of the phosphoranyl radical. On the other hand, the intramolecular migrations of the ligands should abolish this effect. In order to observe the "memory" effect, Hay and Roberts[32] obtained radicals of the type $(RO)_2\dot{P}(OR^1)OR^2$ in two ways: by the reaction between $(RO)_2POR^1$ and $R^2O^\cdot$ and by the reaction between $(RO)_2POR^2$ and $R^1O^\cdot$. The relative yields of the radicals $R^{1\cdot}$ and $R^{2\cdot}$, formed as a result of β-elimination, are independent of the source of the intermediate phosphoranyl radicals. It follows from these date that the tetraalkoxyphosphoranyl radicals do not retain a "memory" of their origin. The authors[32] concluded that the high rate of exchange of the alkoxy-ligands in phosphoranyl radicals precludes the observation of a "memory" effect in reactions involving the oxidation of phosphites by alkoxy-radicals. It follows from the above results[32] that the "memory" effects observed previously by Bentrude and coworkers in the oxidation of phosphites by alkoxy-radicals were not confirmed in their repeated investigations.

Thus the influence of the interchange of ligand positions in phosphoranyl radicals on the yield of the stereoisomers of the final products depends on the rates of these processes and on the rate of decomposition of the phosphoranyl radicals.

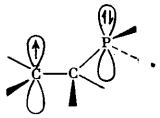
IV. CONFORMATION OF PHOSPHORUS-SUBSTITUTED RADICALS

There exists a wide class of phosphorus-containing radicals in which the unpaired electron is localised at carbon atoms in the β-positions relative to the phosphorus atom. In such radicals the hyperfine interaction of the unpaired electron with the phosphorus nucleus depends significantly on their geometrical structure. Symons and coworkers[33,35] investigated the EPR spectra of the radicals

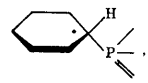


(XLIV) (XLV)

obtained by the γ-irradiation of powdered specimens of the corresponding phosphines and phosphonium salts at 77 K. The isotropic HFI constants calculated from the spectra proved to be $a_P = 251$ G for (XLIV) and $a_P = 120$ G for (XLV). The much higher values of a_P for the former radical can be accounted for by the homoconjugation of the $2p_z$ unpaired electron orbital and the phosphorus orbital occupied by the lone electron pair:

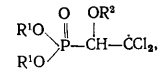


The mechanism of the delocalisation of the unpaired electron over the quadrivalent phosphorus atom in radical (XLV) is not so evident. Presumably the transfer of unpaired electron spin density to the quadrivalent phosphorus atom proceeds via $p_\pi - d_\pi$ conjugation. However, Symons believes[35] that this mechanism is unlikely, since it is inconsistent with the isotropic nature of the HFI constant. As an alternative hypothesis, a hyperconjugation mechanism involving the C–P bond was postulated. The strong hyperfine interaction with the phosphorus nucleus in the cyclohexadienyl radical



obtained by the γ-irradiation of phenylphosphonous acid PhPO(O)H at 77 K, can be accounted for by an analogous mechanism[36]. An isotropic EPR spectrum was observed for this radical and the following HFI constants were calculated from it: $a_H = 40$ G for the methylene proton, $a_H = 10$ G for the *ortho*- and *para*-protons of the benzene ring, and $a_P = 200$ G.

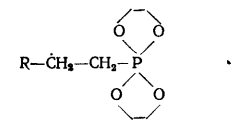
Damerau and coworkers[37–40] obtained radicals of the type



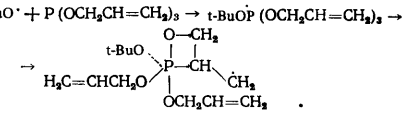
in aqueous solution for which a_P varies from 60 to 69 G, depending on the size of R^1 and R^2, and in addition it depends on temperature. The latter finding is related to the angular dependence of the phosphorus hyperfine interaction constant and constitutes significant evidence in support of the hyperconjugation mechanism[37].

A number of β-phosphorus-substituted alkyl radicals have been obtained in the liquid phase by the addition of phosphorus-centred radicals to unsaturated compounds. For such radicals, the phosphorus hyperfine interaction constant is in the range from 30 to 180 G and is determined mainly by the conformation of the radical. Thus Beckwith[41] investigated the EPR spectra of the radicals formed as a result of the addition of HPO_2, $H\dot{P}O_3$, and $\dot{P}O_3^{2-}$ to unsaturated compounds of the type $R_2C=CR'_2$, where R, R' = H, CH_3, CO_2H, or the aci-anions of nitroalkanes ($H_2C=NO_2$). The phosphorus hyperfine interaction constants in the resulting adducts varied in the range from 60 to 100 G; the phosphorus hyperfine interaction is treated within the framework of the hyperconjugation mechanism with participation of 3*d* orbitals. Radicals of an analogous type were also obtained by Gilbert et al.[42] The phosphorus hyperfine interaction constants in these adducts vary with temperature, which shows that they depend on the conformation.

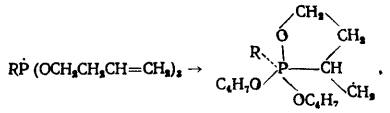
Davies et al.[43] investigated the EPR spectra of the radicals formed following the addition to the double bond of dialkoxyphosphonyl radicals of the type $(RO)_2\dot{P}O$, for which the phosphorus hyperfine interaction constant in the range 94–112 G and this corresponds to β-phosphorus-substituted alkyl radicals. Radicals have been obtained similarly by the addition of spirophosphoranyl radicals to olefins[44]:



Davies et al.[45] also observed an interesting reaction involving the intramolecular addition of the phosphoranyl radical to the double bond of an olefinic substituent. Phosphoranyl radicals containing 2-alkenyloxy-substituents cyclise to oxaphosphotans, in which the unpaired electron is localised at an exocyclic carbon atom:



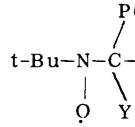
Depending on the substituents, a_P varies from 176 to 199 G. On the other hand, if the phosphorus atom is linked to 3-alkenyloxy-groups, cyclic oxaphospholan radicals are formed;



for which the isotropic HFI constant is $a_P = 127-136$ G.[45]

From the standpoint of conformational analysis, more or less stable nitroxy-radicals incorporating phosphorus-containing fragments proved to be very interesting. Il'yasov and coworkers[46] obtained a large number of such radicals using 2-methyl-2-nitrosopropane as the spin-trapping agent and analysed in detail their EPR spectra. The presence of one or two magnetic phosphorus nuclei in nitroxy-radicals of this kind leads to the appearance of hyperfine interaction of the unpaired electron with these nuclei; the HFI constant can serve as a criterion of the conformation of the molecules and of its dependence on the steric and electronic effects of the substituents. Additional information is provided by the hyperfine interaction β-proton constant when a β-proton exists.

Table 1. The HFI constants for radicals of the type



obtained in a 1:3 (by volume) water–alcohol mixture at room temperature.

No.	Y	a_N, G	a_P, G	a_H, G
(XLVI)	$P(O)(OEt)_2$	14.2	42.1; 42.5	1.6
(XLVII)	H	16.3	45.0	10.3 (2H)
(XLVIII)	COOMe	14.3; 14.2	29.2; 28.8	2.0; 2.4
(XLIX)	COOEt	14.3; 14.3	28.7; 28.5	2.3; 2.5
(L)	$COOC_3H_7$	14.3; 14.3	28.8; 28.4	2.4; 2.8
(LI)	COC_6H_5	14.3; 14.3	22.6; 22.5	4.7; 4.8

Table 1, taken from the paper by Il'yasov and coworkers[46], lists the EPR data for nitroxy-radicals with phosphorus-containing fragments. We shall consider the nitroxy-radical (XLVI), which incorporates two phosphorus atoms. The presence of two different ^{31}P hyperfine interaction constants and the low value of the single β-proton hyperfine interaction constant ($a_H = 1.6$ G) are striking. These data agree with the conformation proposed by the authors[46], which has the form, in terms of the Newman projection, illustrated in Fig.1. The low values of the β-proton hyperfine interaction constant shows that the angle between the direction of the C–H bond and the axis of the $2p_z$ orbital of the unpaired electron is close to 90° ($\alpha \to 0$). For the same reason, the difference between the two phosphorus hyperfine interaction constants is only 0.4 G. With increase of temperature, the phosphorus HFI constants become even more similar but the complete equivalence of the two phosphorus nuclei could not be attained up to 100 °C. A further increase of temperature is limited owing to the inadequate stability of the radical.

For the phosphononitroxy-radical (XLVII), which has one phosphorus atom and two β-protons, there is a complete equivalence of the protons even at room temperature. It might have been thought that the equivalence of the two protons is due to the free rotation of the $C(P)H_2$ fragment about the C–N bond. However, the experimental value of the constant $a_H^\beta = 10.3$ G, the lower limit of which is 13 G according to Chapelet-Letournux et al.[47], is inconsistent with this hypothesis. In order to account for the equivalence of the β-protons in radical (XLVII), the authors[46] therefore postulated a rapid transition between two conformations, which would lead to the averaging of the hyperfine interaction with the protons H_a and H_b (Fig.2).

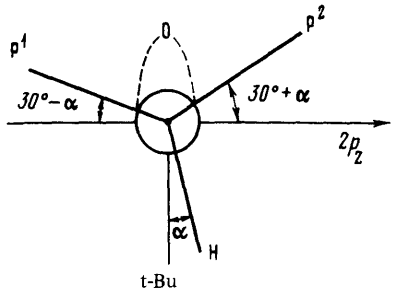


Figure 1. Schematic representation of one of the conformations of the nitroxy-radical (XLVI).

The two conformations are energetically equivalent and the average value of a_H under the conditions of a rapid transition is therefore determined by the simple relation:

$$\langle a_H \rangle = \frac{1}{2} B_2^N \rho_N^\pi (\langle \cos^2 90° \rangle + \langle \cos^2 30° \rangle)$$

where $\beta_2^N \rho_N^\pi = 26 \pm 2$ G is characteristic of the majority of nitroxy-radicals[47].

Stone and Maki[48] developed a theory, according to which the the values of $\langle \cos^2\theta \rangle$ are related to the barrier V_0 to the conformational transitions. Using conclusions from this theory, Il'yasov and coworkers[46,49] showed that the experimental β-proton hyperfine interaction constant in radical (XLVII) $a_H^\beta = 10.3$ G corresponds to the barrier $V_0 = 2$ kcal mole^{-1}.

Table 1 shows that a_P for the phosphononitroxy-radicals (XLVIII)–(LI) is greatly reduced compared with the values for radicals (XLVI) and (XLVII), which indicates an increase of the angle θ_P, which can be estimated from the β-proton splitting. For example, $\langle \theta_H \rangle = 80°$ when $V_0 = 3$ kcal mole^{-1} has been found for the nitroxy-radical (L) from the expression

$$a_H^\beta = \rho_N^\pi (B_0 + B_2 \langle \cos^2 \theta_H \rangle)$$

on the assumption that $B_0 \cong 0$ [50] and using the experimental value $a_H^\beta = 2.8$ G. Here it is evident that $\langle \theta_P \rangle = 40°$. The expression

$$a_P^\beta = \rho_N^\pi (B_0 + B_2^P \langle \cos^2 \theta_P \rangle)$$

with $B_0 \cong 0$ and $\rho_N^\pi B_2^P = 56$ G [46] yields $a_P = 31$ G, which is very close to the experimental value $a_P = 28.8$ G.

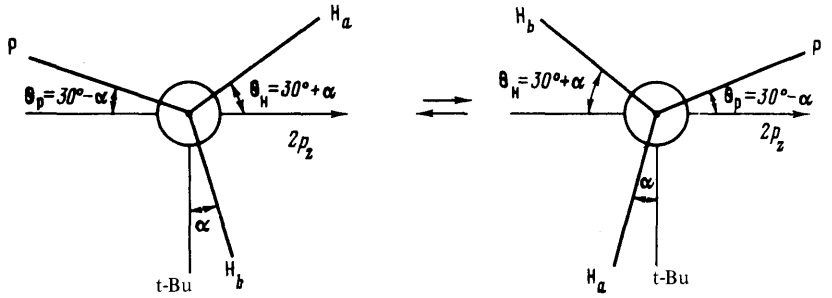
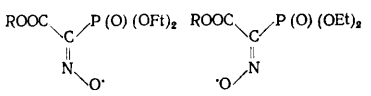


Figure 2. Schematic illustration of the conformational transitions in the nitroxy-radical (XLVII).

With decrease of temperature, the EPR spectra of the two forms of the nitroxy-radicals (XLVIII)–(LI) are resolved. In their study of the temperature dependence of the concentration of the two forms, Il'yasov and coworkers[46] estimated the difference between the energies of these forms. Thus $\Delta H = -0.36$ and -0.77 kcal mole^{-1} for radicals (XLVIII) and (L) respectively.

The unpaired electron in the nitroxy-radicals examined above is localised mainly in the 2*p* orbitals of the nitrogen and oxygen atoms. The angular dependence of the ^{31}P hyperfine interaction constant shows that the transfer of spin density to the phosphorus atom proceeds via the hyperconjugation mechanism.

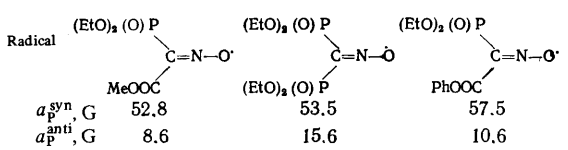
Il'yasov and coworkers[51] obtained phosphorus-containing iminoxy-radicals of another type:



(LII)

A characteristic feature of these radicals is the possibility of spin density transfer to the phosphorus atom via the system of σ bonds, since the unpaired electron is located mainly in the σ plane. The EPR spectra showed that in solution the radicals (LII) exist in the form of stable *syn*- and *anti*-isomers with markedly different HFI constants and *g*-factors. The spectroscopic parameters of some of the radicals investigated are listed in Table 2, which shows that the phosphorus hyperfine interaction constant is much greater for the *syn*-isomers than for the *anti*-isomers. The authors[51] found from the temperature dependence of the relative concentrations of the isomers that the equilibrium is displaced towards the *anti*-isomer, which is thermodynamically more favourable ($\Delta H = -1.1$ kcal mol^{-1}).

It is interesting to compare the influence of the electronic properties of substituents on the phosphorus hyperfine interaction constant in the *syn*- and *anti*-isomers. For this purpose, we shall compare the values of a_P for the following three radicals[49]:



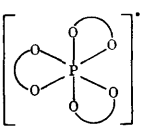
The data show that the electronic properties of the substituents have a greater influence on the a_P constants for the *anti*-isomers. One can therefore postulate that in these isomers the σ–π polarisation and the delocalisation of the unpaired electron over the σ bonds make a significant contribution to the phosphorus hyperfine interaction. In the *syn*-isomers the spin density is largely transmitted via a mechanism involving the direct overlap of the orbitals of the unpaired electron with the σ orbitals of the C–P bond.

Table 2. Parameters of the EPR spectra of radicals (LIII).

R	Isomer	a_N	a_P	g^{iso}
Me	*syn*	32.4	52.8	2.0038
	anti	32.4	8.6	2.0041
Et	*syn*	32.5	52.9	2.0038
	anti	32.8	8.5	2.0041
Pr	*syn*	32.3	53.0	2.0038
	anti	32.3	8.6	2.0041

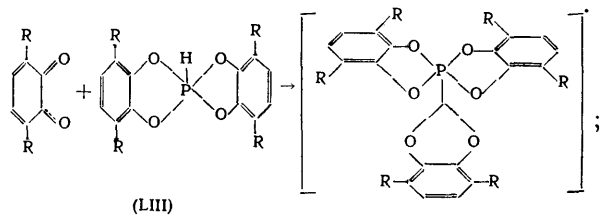
V. TAUTOMERISM OF PHOSPHORANYLPHENOXY-RADICALS

The previous sections dealt with radicals in which the free valence was localised either in the hybrid orbitals of the phosphorus atom (phosphoranyl radicals) or in the *p* orbitals of the carbon or oxygen atoms linked directly to the phosphorus atom. Here we shall deal with radicals where the free valence migrates between the oxygen atoms of catechol ligands attached to the phosphorus atom. In these radicals the phosphorus is formally hexacoordinate[8]:



The arcs drawn between two oxygen atoms represent different *ortho*-phenylene groups[53]. The migration of the free valence in these radicals involves the stereochemical features of quinquevalent phosphorus (see above).

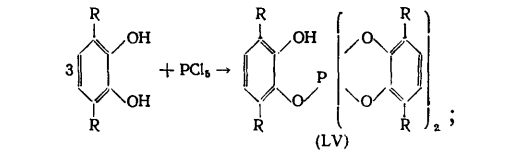
The photoinitiated reaction of 3,6-di-t-butyl-o-quinone with the spirophosphorane (LIII) leads to the formation of an analogue of the phosphate anion (LIV) which carries an unpaired electron instead of a negative charge[8]:



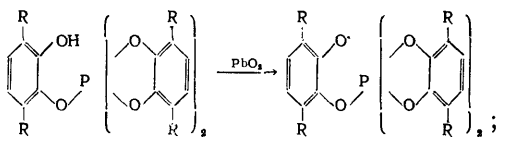
(LIII) (LIV)

R = t-Bu.

The same free radical can be obtained by the oxidation with lead dioxide of the hydropyrophosphorane (LV), which is synthesised in its turn from 3,6-di-t-butylcatechol and phosphorus pentachloride[58]:



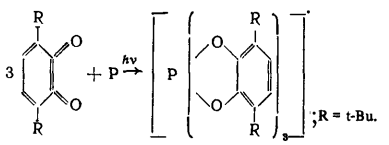
(LV)



(LIV)

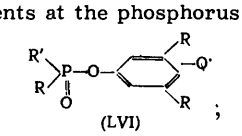
R = t-Bu.

Radical (LIV) is also obtained by the photoaddition of 3,6-di-t-butyl-o-quinone to elemental phosphorus[53]



R = t-Bu.

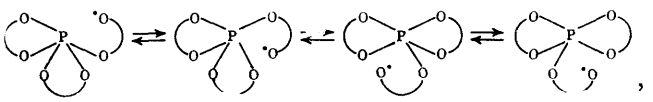
Solutions of the free radicals (LIV), obtained in different ways, exhibit identical EPR spectra with similar temperature variations. Fig. 3 illustrates the EPR spectrum of radical (LIV) in ether. At 20 °C the spectrum consists of a doublet with a phosphorus splitting of 4.0 G; each component of the doublet consists of seven lines with the intensity ratios 1 : 6 : 15 : 20 : 15 : 6 : 1 (the splitting by the six equivalent protons is $a_H = 1.45$ G). Thus the unpaired electron interacts with all six protons of the three benzene rings and with the phosphorus atom. The spin density at the phosphorus atom itself is then low: the splitting constant of 4.0 G can be compared with the splitting in the spectrum of the phenoxy-radical (LVI), which amounts to 6–7 G (depending on the nature of the substituents at the phosphorus atom):[52]



(LVI)

R = t-Bu.

One must assume that the unpaired electron spin density is localised mainly in the catechol fragments. With decrease of temperature, the components are broadened at −80 °C the spectrum is converted into a doublet of triplets (Fig. 3)—a doublet due to the phosphorus atom and a triplet with a splitting of 4.35 G due to the two protons of one ring[8,53]. Thus at 20 °C and above the free valence "migrates" between all six equivalent oxygen atoms:



etc., while at low temperatures the EPR spectra reveal the interaction with the protons of only one ring.

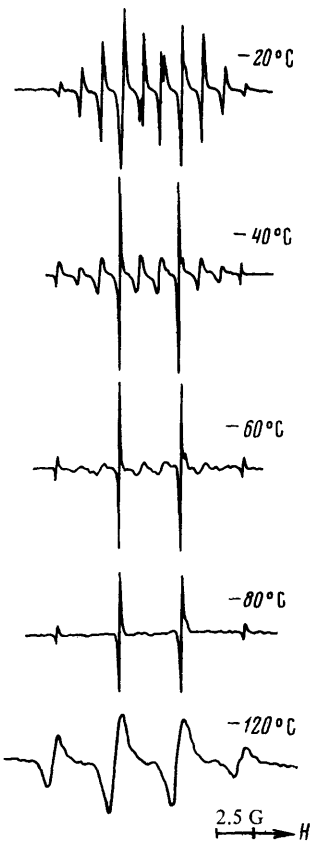


Figure 3. The EPR spectrum of radical (LIV) in ether at different temperatures.

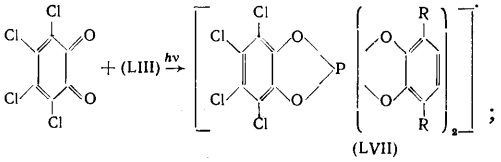
The temperature-induced changes in the spectrum have been studied in greater detail in solution in ether[53]. At low temperatures a quartet splitting was observed (by two protons and a phosphorus atom; 1 : 3 : 3 : 1), but the intermediate spectra are particularly distinct and convenient for the kinetic analysis of the exchange process. It was found that, with decrease of temperature, both interligand and intraligand exchange reactions are retarded to approximately the same extent, but, whereas the interligand exchange is already "frozen", the rapid-exchange spectral conditions are maintained for the intraligand exchange, which

has approximately the same intrinsic frequency, and we observe splitting by two protons. The exchange frequency is

$$\nu_{exch}=3.4\cdot10^{12}\exp[(-4300\pm500)/RT]\ s^{-1}.$$

The frequency of the "migration" of the unpaired electron at 20 °C (toluene) is $2.2\times10^9\ s^{-1}$. Thus at 20 °C the unpaired electron passes through all six oxygen atoms with a jump frequency of 2×10^9 per second.

The interaction of the spirophosphorane (LIII) with *o*-chloranil on irradiation also gives rise to the radical (LVII), which contains a formally hexacoordinate phosphorus atom[8]:

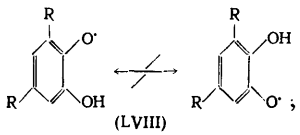


(LVII)

R = t-Bu.

The presence of four chlorine atoms in a single ring suggested that the unpaired electron spin density is preferentially concentrated in two other catechol fragments and at the phosphorus atom. Indeed the 1:3:3:1 quartet is observed in the EPR spectrum at −80 °C (splitting by the phosphorus atom and the two protons—interaction of the unpaired electron with the protons of a single ring), while on increase of temperature the spectrum is transformed into a doublet of 1:4:6:4:1 quintets corresponding to four equivalent protons. The splitting by phosphorus is 4.35 G and that in the quintet is 2.18 G#. It is remarkable that the splitting in the quintet is 1.5 times greater than that (1.45 G) in the septet and the symmetrical radical (LIV). The explanation is that the same spin density in the former case is distributed over six protons, while in the latter case it is distributed over four protons. Hence the entire spin density, previously distributed over three ligands, is now concentrated in two ligands, i.e. we have a "four-well" system[8].

Hitherto we have considered only radicals with a symmetrical ligand—the 3,6-di-t-butylphenylenedioxy-group. A series of studies have been carried out with an asymmetric ligand—the 3,5-di-t-butylphenylenedioxy-group. In the first place one should note that neither hydrogen nor deuterium migrate in the corresponding semiquinone radical—the 4,6-di-t-butyl-2-hydroxyphenoxy-radical (LVIII)—up to 200 °C:[54]

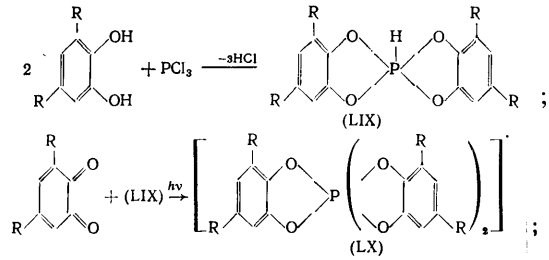


(LVIII)

R = t-Bu.

From our point of view, this can be explained by the non-equivalence of the oxygen atoms; the transfer of the proton to the oxygen atom adjoinging the t-butyl group actually becomes relatively unfavourable owing to the steric shielding by this group§. One could therefore assume that there is no intramolecular exchange in "multiwell" systems containing this fragment.

The photoinitiated reaction of 3,5-di-t-butyl-*o*-quinone with the spirophosphorane (LIX), obtained from 3,5-di-t-butylcatechol and phosphorus trichloride, leads to the formation of the free radical (LX) with three 3,5-di-t-butylphenylenedioxy-ligands[56]:

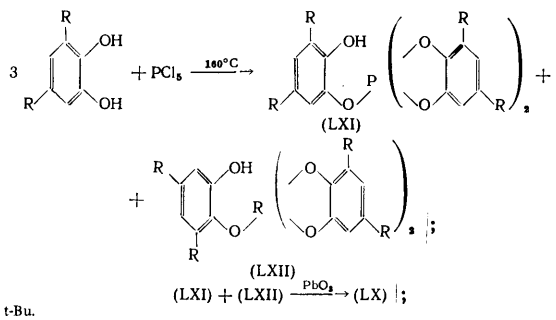


(LIX)

(LX)

R = t-Bu.

The same radical is formed in the oxidation with lead dioxide of a mixture of the spirophosphoranes (LXI) and (LXII) obtained from 3,5-di-t-butylcatechol and phosphorus pentachloride. When these reactants are fused together, a mixture of the isomers (LXI) and (LXII) is produced; on oxidation, both isomers give rise to the same three-ligand radical (LX):[56]

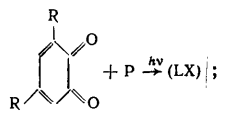


(LXI)

(LXII)

R = t-Bu.

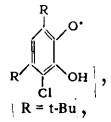
The same radical is formed in the photoinitiated reaction of elemental phosphorus with 3,5-di-t-butyl-*o*-quinone[53]:



R = t-Bu.

At a low temperature (−100 °C, toluene) the EPR spectrum of this radical consists of a triplet due to the hyperfine interaction with the proton in the 5-position and the phosphorus

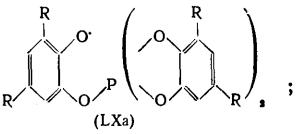
§ This does not imply that the absence of symmetry in the radical inevitably leads to the absence of migration. This happens only for large energy differences between different forms. In other cases, for example, for the 4,6-di-t-butyl-3-chloro-2-hydroxyphenoxy-radical



all the characteristics of hydrogen-tropic tautomerism[55] (non-degenerate!) are observed.

Radical (LVII) is unstable and disproportionates even at −40 °C, which complicates the spectrum.

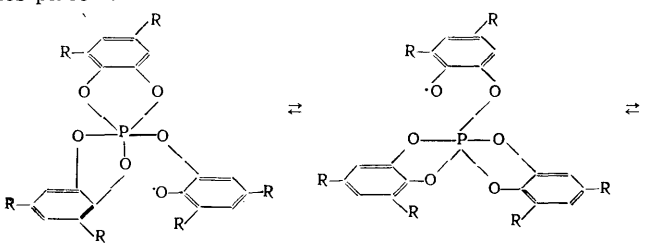
atom ($a_H^5 = a_P = 4.35$ G). Under these conditions, the structure (LXa), with the unpaired electron localised at one of the oxygen atoms of one of the ligands, should be assigned to this radical:

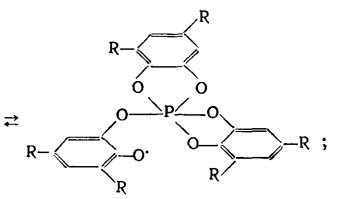


(LXa)

R = t-Bu.

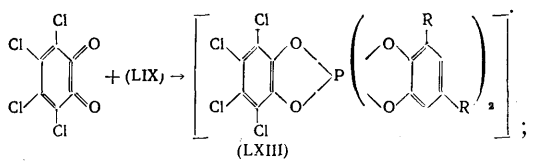
With increase of temperature, additional broad lines appear and at −40 °C a doublet of 1:3:3:1 quartets arises (a_H = 1.45 G)—the unpaired electron interacts with three equivalent protons of three benzene rings; this is a "three-well" system, with one well for each ligand, and only interligand exchange takes place[56]:





R = t-Bu.

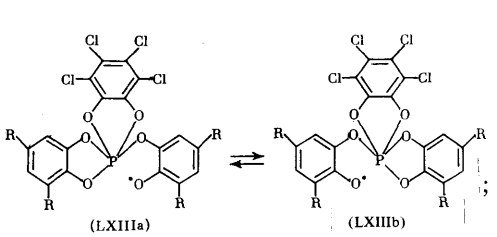
If *o*-chloranil is involved in the reaction with the spirophosphorane (LIX) instead of di-t-butyl-o-quinone, a new three-ligand radical (LXIII) is formed[56]:



(LXIII)

R = t-Bu.

As noted previously, the *o*-chloranil ligand is in this case excluded from the exchange. The EPR spectrum at −100 °C in toluene therefore shows a 1:2:1 triplet ($a_H^5 = a_P = 4.35$ G) and at −40 °C a doublet of 1:2:1 triplets ($a_H = 2.17$ G). In the first case there is a "frozen" structure (LXIIIa) or (LXIIIb), while in the second case there is rapid interligand exchange with splitting by one proton in each ligand:



(LXIIIa) (LXIIIb)

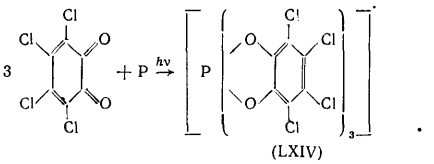
R = t-Bu.

For the low-temperature spectrum (splitting by one proton), the splitting constant is 4.35 G and in the "two-well" system at −40 °C it amounts to 2.17 G, i.e. the splitting by each proton is smaller by a factor of two, while in the "three-well" system the contant is 1.45 G, i.e. the splitting is smaller exactly by a factor of three[56].

The exchange process involving thse radicals belongs to the category of rapid processes. At 20 °C the exchange frequency is 1.2×10^9 s^{-1} for the "three-well" system and 4×10^9 s^{-1} for the "two-well" interligand system[56]. The kinetic parameters of the exchange reactions (s^{-1}) are as follows:

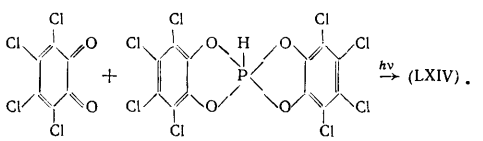
$$\nu_{(LX)} = 4.8 \cdot 10^{12} \exp\{-(4800 \pm 500)/RT\}\ s^{-1};$$
$$\nu_{(LXIII)} = 2 \cdot 10^{14} \exp\{-(6300 \pm 500)/RT\}\ s^{-1}.$$

The reaction of white phosphorus with *o*-chloranil under irradiation gives rise to the highly chlorinated three-ligand radical (LXIV):[53]



(LXIV)

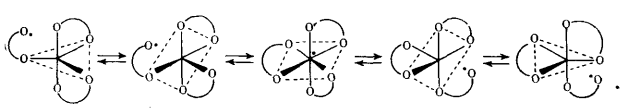
The same radical is formed in the photochemical reaction of *o*-chloranil with a perchlorospirophosphorane:



The EPR spectrum of this radical naturally contains only one doublet with a splitting of 3.4 G by the phosphorus atom, because the hyperfine interaction with the chlorine nuclei is not manifested. Nothing can be said about the characteristic features of this radical.

The examples of the free valence and bond exchange reactions examined involve intramolecular radical substitution at a pentacoordinate phosphorus atom of the "synchronous" type[57]. The instantaneous structure of the given radicals, with the localisation of the unpaired electron at one oxygen atom, consists of a trigonal bipyramid. The pseudorotation characteristic of pentacoordinate phosphorus compounds, as a result of which the apical and equatorial positions change places, has a broad frequency spectrum which depends on the nature of the substituents in these compounds. In particular, the pseudorotation frequencies for hydroxyspirophosphoranes are $>10^5$ s^{-1} and the energy barrier is <8 kcal $mole^{-1}$.[10]

Thus the kinetic equivalence of the intra- and inter-ligand exchange processes can be indissolubly linked to pseudorotation. When the trigonal bipyramid passes through the stage of a tetragonal pyramid on pseudorotation, it is attacked from the "rear" (from the side of the base) by an oxygen atom with an unpaired electron. The intermediate octahedral structure constitutes in this case a transition state[53]:



bipyramid pyramid octahedron pyramid bipyramid

If the pseudorotation frequency is higher than the rate of intramolecular exchange, then any oxygen atom can be located at the apical positions of the bipyramid or at the

vertex of the tetragonal pyramid (positions subjected to radical attack). Evidently the intra- and inter-ligand exchange reactions should be indistinguishable from this point of view. However, it can be assumed that the octahedral configuration constitutes a transition state in which all the oxygen atoms become equivalent and the loss of any of them is equally probable, which is consistent with experimental data; the requirement for high pseudorotation frequencies of the bipyramid then loses significance. Both concepts are evidently fairly speculative in view of the lack of correct pseudorotation frequencies for pentacoordinate phosphorus compounds (above 10^5 s^{-1}). One can only say that the low phosphorus HFI constant and the similarity of the unpaired electron density distribution in the radicals under consideration (when the interligand exchange is "frozen") to that in semiquinone radical-anions with a similar structure indicates the localisation of the unpaired electron almost entirely in the catechol ligand. This constitutes important evidence in support of an octahedral transition state in the intramolecular free valence and bond exchange reactions considered.

The above mechanism apparently determines the nature of the exchange involving radicals containing non-equivalent and asymmetric ligands. The intra- and inter-ligand exchange processes are then manifested as a result of radical attack on the phosphorus atom and the equal probabilities of the appearance of a free valence at any of the oxygen atoms (for symmetrical and identical ligands).

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