CONCLUSIONS

1. Direct proof for the phosphorotropic tautomerism, where compounds with a pentacoordinated phosphorus atom are in equilibrium, was obtained from the comparative analysis of temperature dependences of ¹³C and ³¹P NMR spectra of phosphoranes containing 1,3,2-dioxa- and 1,3,2-oxazaphospholene rings, and related bipolar ions.

2. Free energies of activation of the phosphorotropic rearrangement were determined.

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ESR SPECTRA OF PHOSPHONYLTHIO-SUBSTITUTED ETHYL RADICALS

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In recent years, various organic and heteroorganic radicals have been shown to be capable of adding to the sulfur atoms of the C=S bond in thicketones, thicamides, and other thiccar-bonyl compounds [1]. In our recent work [2], we described a preparative and ESR spectroscopic study of the addition of phenyl and methyl radicals to O-esters of thiccarboxylic acids. The addition of phosphonyl radicals at C=S bonds has not been reported. In light of the ease of addition of these radicals at the C=C bond [3], it was of interest to study their reaction with thiccarbonyl compounds.

In the present work, we studied the radicals obtained in the addition of various phosphonyl radicals to 0-phenyl esters of phenylthioacetic and diphenylthioacetic acids as well as to nitrogen-substituted diphenylthioacetamide derivatives.

The phosphonyl radicals were obtained by the photolysis of solutions of the corresponding hydrophosphoryl compounds in a mixture of pentane and tert-butyl peroxide [4]. ESR signals of substituted ethyl radicals were detected upon the addition of thiocarbonyl compounds to the reaction mixture and UV irradiation, which indicated the addition of phosphonyl radicals at the sulfur atom. The reaction proceeds as follows:



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TABLE 1. Hyperfine Coupling Constants in the ESR Spectra of Phosphonylthio-Substituted Radicals



								North Real Property of the
					ap	a _H		- 10
Radical	R1	R²	R3	R4	Oe		e	т., ч
				_				50
(I)	Ph	OEt	OEt	OPh	77,0	14,9	57°	
(II)	Ph	CH ₂ CH ₂ Cl	Ph	OPh	70,0	13,6	. 58°	-30
(III)	Ph	0-CH < He Me	Ph	OPh	65,3	13,6	58°	-20
(IV)	Ph)-CH	Ph	OPh	65,7	13,0	59°20′	-40
(V)	Ph	OCH₃	Ph	OPh	65,0	13,28	59°	-40
(VI)	Ph	OEt	Ph	OPh	64,4	12,8	58°	-40
(VII)	Ph	Ph	Ph	OPh	55,4	11,3	61°36′	+20
(VIII)	Ph	OH	Ph	OPh	58,7	9	64°54′	+20
(IX) *	Ph	OCH ₃	Ph	OPh	78,2	28,9	40°6′	-40
(X)	н	OEt	OEt	OPh	85,5	$a_{\rm H^1} = a_{\rm H^2} = 16,6$	54°8′	+20
(XI)	н	OEt	Ph	OPh	73,0	$a_{\rm H^1} = 15,2$ $a_{\rm H^2} = 17,0$	56°28′ 54°40′	+20
(XII)	н	Ph	Ph	OPh	62	$a_{\rm H^1} = a_{\rm H^2} = 15,2$	56°28′	+20
(XIII)	Ph	Me O-CN Me	Ph	NHPh	· 88 ,2	23,2 †	47°56′	-50
(XIV)	Ph	OEt	OEt	NEt ₂	120,0	22,7 ‡	47°18′	-70

*P=S bond instead of P=0 bond.

[†]Coupling was detected with the ¹⁴N nucleus, $a_{\rm N} = 3.8$ Oe. [‡]Coupling with the ¹⁴N and H nuclei was detected: $a_{\rm N} = a_{\rm H} = 5.2$ Oe.



The hyperfine coupling constants with the nuclei of the phosphorus atoms and β -hydrogen atoms are given in Table 1. Analysis of these coupling constants and the temperature dependence of the ESR spectra showed that these radicals have rather rigid conformations. Table 1 also gives the torsional angles θ between the C-H bond and the axis of the 2p orbital of the unshared electron in the ethyl radical. Angle θ was calculated using the equation,

$a_{\rm H} = B \cos^2 \theta$

where B = 50 Oe [5].

Figure 1 shows the temperature dependence of the ESR spectrum of the 1-(diethoxyphosphonylthio)-l-phenoxy-2,2-diphenylethyl radical (I). The observed alternation of the linewidth with a decrease in the temperature is related to a decrease in the frequency of transition between conformations with similar angle θ . Analysis of the splitting shows that there is a slight increase in the coupling constants with the phosphorus and β -hydrogen nuclei with decreasing temperature.

Diagrams d and e in Fig. 1 show the different position of the ESR lines of ESR spectrum c relative to the positions of the lines in spectrum a. The large interval ΔH_1 causes a sharp increase in the end components in accord with the equation describing the linewidth Γ



Fig. 1. ESR spectra of radical (I): a) +50°C, $a_{\rm P} = 76.5$, $a_{\rm H} = 14.3$ Oe, b) +10°C, $a_{\rm P} = 76.2$, $a_{\rm H} = 15.3$ Oe, c) -30°C, $a_{\rm P} = 76.0$, $a_{\rm H} = 17.0$ Oe, d) diagram of the spectrum at +50°C, e) diagram of the spectrum at -30°C. ΔH_1 and ΔH_2 are intervals characterizing the different position of the lines in spectrum c relative to spectrum a.

in terms of rapid exchange [5]:

$$\Gamma = \Gamma_0 + \gamma \frac{\tau \, (\Delta H)^2}{4}$$

Analysis of the temperature dependence of the linewidths permitted estimation of the barrier separating these conformations, which was found to be 2 ± 0.5 kcal/mole. The observed alternation pattern indicates that the displacements of the C-H and S-P bonds relative to the orbital of the unshared electron are synchronous.

Our hypothesis that the conformations involved in the transitions differ only slightly relative to the value of angle θ is supported by analysis of the spectrum of the 1-[pheny1-(sec-butoxy)phosphonylthio]-1-phenoxy-2,2-diphenylethyl radical (III). The transition rate is decreased upon a reduction in temperature to an extent permitting us to record the ESR spectra of the separate conformers (Fig. 2). The coupling with the hydrogen and phosphorus nuclei in these conformations differs only slightly. In the range from -40° to $+100^{\circ}$ C, the coupling with the phosphorus nucleus is determined by the equation: $a_{\rm p}{}^{\rm I}{}_{\rm m_1} + a_{\rm p}{}^{\rm I}{}_{\rm m_2} = a_{\rm p}$, where $a_{\rm p}$ and $a_{\rm p}{}^{\rm II}$ are the corresponding coupling constants and ${}_{\rm m_1}$ and ${}_{\rm m_2}$ are the mole fractions of the conformations. This equation was used to find the enthalpy difference between these two conformers ($\Delta H = 5.5 \pm 1 \text{ kcal/mole}$). Determination of the enthalpy difference between the two conformers related to hindered rotation of the CHPh2 group using the temperature dependence of the coupling constants with the hydrogen atom gives a value of 8.4 ± 1 <code>kcal/mole. The similarity of the values</code> of ΔH related to the conformational transitions of the different groups in the radical may be seen as an indication that these transitions are interrelated and a function of the same barrier. It is interesting that the linewidth alternation noted above is found for conformation I. This indicates that there is an additional conformation near this conformation which is separated by a low barrier. The transition between these conformations is apparently accompanied by the same behavior of the coupling constants as in radical (I).



Fig. 2. ESR spectra of radical (III) at a) +70°, b) -40°, c) -50°, d) -60°C. Arrows 1 and 2 indicate the position of the hyperfine coupling lines in the ESR spectra of the two conformers. The middle arrows indicate the positions of the phosphorus doublets. $a_{p1} = 59.2$, $a_{p2} = 66.7$, $a_{H1} = 12.9$, $a_{H2} = 11.6$ Oe.



Fig. 3. ESR spectrum of radical (XI) at room temperature.

Figure 3 shows the ESR spectrum of 1-[pheny1(ethoxy)phosphonylthio]-1-phenoxy-2-pheny1ethyl radical (XI), in which a clear difference is seen between the coupling constants of the $two positionally nonequivalent <math>\beta$ -hydrogen atoms. The calculated values of θ_1 and θ_2 permit us to draw the following Newman projection of this radical



The values for θ found for most other radicals are close to θ_1 and θ_2 . The splitting due to the phosphorus atom is undoubtedly determined by hyperfine coupling similar to that for the β -hydrogen atoms although the parameter B in the equation $a_p = B\cos^2\theta$ is unknown and the data in Table 1 give only the trend for change in angle θ in this series of radicals. For most radicals, a decrease in a_p is found with increasing temperature:

$$a_{\rm P} = a_{\rm P}^{\circ} (0^{\circ} \text{ C}) - (0.03 \pm 0.01) \text{Oe}^{\circ} \text{C}$$



Fig. 4. Upfield component of the phosphorus doublet in the ESR spectrum of radical (XIV) at -70 °C.

TABLE 2. Coupling Constants with the ${}^{31}P$ Nucleus in RR ${}^{1}P = 0$ Radicals

R	\mathbf{R}^{1}	a₽,Oe	R	\mathbb{R}^1	۵p, Oe
EtO Ph Ph Ph Ph	EtO Ph EtO <i>i</i> -PrO	700 390 484 482	Ph Ph Ph * Ph	sec-BuO MeO MeO ClCH ₂ CH ₂ O	482 484 392 490

*Ph(MeO)P=S radical.

In most cases [(II), (III), (IV), (V), (VI) and (IX)], spectra for two conformers are detected at low temperature. We also studied the ESR spectra of 1-phenyl(isopropoxy)phosphonylthio-1-phenylamino-2,2-diphenylethyl and 1-(diethoxyphosphonylthio)-1-diethylamino-2,2-diphenylethyl radicals, (XIII) and (XIV), respectively.

Figure 4 gives the ESR spectrum of radical (XIV) at -70 °C.

The hyperfine structure may be interpreted if we assume equal coupling constants of the unpaired electron with the nitrogen nucleus and the two hydrogen atoms of the CH_2 fragment of one of the ethyl groups. In this case, a quintuplet with 1:3:4:3:1 line intensity ratio should arise in addition to the doublets related to the phosphorus and β -hydrogen nuclei. A similar intensity ratio is observed in the quintuplet in Fig. 4.

EXPERIMENTAL

The phosphonyl radicals were obtained by the reaction of tert-butoxyl radicals generated by photolysis with hydrophosphoryl compounds using a DRSh-250 M lamp (the tert-butyl peroxide: pentane:phosphate ratio was 60:38:2). The formation of phosphonyl radicals was confirmed by detection of their ESR spectra. Table 2 gives the hyperfine coupling constants with the phosphorus nucleus with values characteristic for phosphonyl radicals [4].

The phosphonyl radicals disappeared upon the addition of 0.5% thioacetic acid derivative and were replaced by phosphonylthio-substituted ethyl radicals. The ESR spectra were measured at from -80° to $+100^{\circ}$ C in evacuated quartz ampuls on a Varian E-12A spectrometer. The synthesis of the starting compounds were described in our previous work [6, 7] and by Pudovik and Yarmukhametova [8].

CONCLUSIONS

1. An ESR study of phosphonylthio-substituted thioethyl radicals indicated the favored conformations and gave the barriers and enthalpies of the transitions between these conformations.

2. A synchronous mechanism was proposed for the rotation of the hindered methyl and thiophosphonyl groups in the conformational transitions in these radicals.

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ESR SPECTRA OF SOME PHOSPHONIMINOXYLS

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Phosphorus-containing iminoxyl radicals first described in our previous work [1] were generated as secondary products in the photolysis of a solution of 2-methyl-2-nitrosopropane in the presence of alkyl esters of phosphonyl- α -iodoacetic and phosphonyl- α -bromoacetic acids. In subsequent work [2-4], we described phosphoniminoxyls with β - and γ -phosphorus atoms relative to the C=NO radical site formed in photochemical and electrochemical reactions. As in the case of other iminoxyl radicals, phosphorus-containing iminoxyls exist in stable syn and anti forms with markedly different coupling constants with the phosphorus atom and other magnetic nuclei. ¹H and ³¹P NMR and IR spectroscopic studies showed that these radicals exist as syn and anti isomers and some of the isomeric forms are stabilized by intramoleuclar interactions [5].

In order to obtain further clarification of intramolecular interactions in phosphoniminoxyls and establish the effect of the immediate environment at the phosphorus atom and the radical site, an ESR study was carried out on a series of phosphorus-containing iminoxyls (Table 1) obtained by the oxidation of the corresponding phosphorylated oximes by a method described below. The characteristic ESR spectrum of phosphoniminoxyl (III) is given in Fig. 1. The ESR spectra of phosphorus-containing iminoxyl radicals consist of two groups, each of which of six hyperfine structure lines due to the coupling of the unpaired electron with the ¹⁴N and ³¹P nuclei in the two isomeric forms of the radical. The ESR parameters of the phosphoniminoxyls studied are given in Table 1. The coupling constants (a_p) and g-factors for the syn and anti isomers differ significantly. Confirmation that the observed spectra are related to two isomeric forms of the radical is the reversible change in the intensities of the two groups of ESR lines with change in the temperature and the dependence of the ratio of the line intensities for these groups on the nature of the solvent. Figure 2 gives the tempera-

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