NEW PHOSPHORUS-CONTAINING PHENOXYL RADICALS

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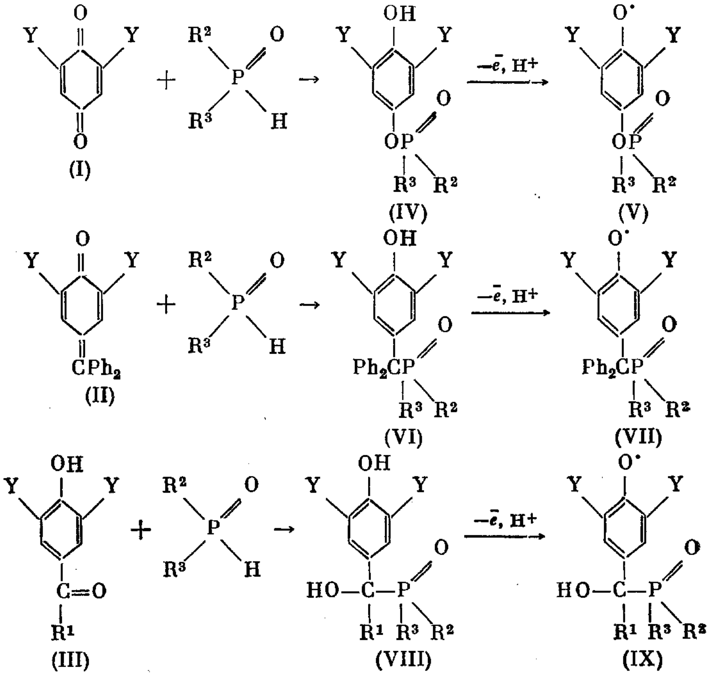
Organophosphorus compounds with a labile P—H bond readily add to the C=O group with the formation of the corresponding hydroxyl compound [1]. In the present work, we used this reaction to obtain phosphorus-containing, sterically hindered phenols and phenol radicals. The interest in these radicals is a consequence of the feasibility of investigating the effect of structure in the spectra of these species. In addition to the ordinary questions of hindered rotation of phosphorus-containing fragments about P—O and P—C bonds, it is also possible to study the stereoisomeric relationships between individual groups in the radicals formed. In particular, if there are two asymmetric centers in the radicals formed, then diastereomeric effects in the ESR spectra of the corresponding radicals may be studied.

In studies on diastereomerism and diastereotopy, there have been only a few reports [2, 3] of different coupling constants in the ESR spectra of several nitroxyl radicals in the case of diastereomers or diastereotopic nuclei (protons). The difficulties in finding suitable objects of investigation are due to the requirement of significant coupling constants at the nuclei of the asymmetric centers. This condition is met by the phosphorus-containing phenoxyl radicals studied in the present work: 2,6-di-tert-butyl-p-benzoquinone (I), 2,6-di-tert-butyl-α,α-diphenylmethylenequinone (II), 2,6-di-tert-butyl-4-formylphenol (IIIa), 2,6-di-tert-butyl-4-acetylphenol (IIIb), and 2,6-di-tert-butyl-4-acetoacetylphenol (IIIc). It was expected that the reaction of these compounds with compounds containing a



Y = *t*-Bu; R^1 = H (a), CH_3 (b), CH_2COCH_3 (c).

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TABLE 1. Coupling Constants in the ESR Spectra of Phosphorus-Containing Phenoxyl Radicals in Diethyl Ether at 20°C

Phenoxyl	R^2	R^3	$a_{^{31}P}$	$a_{m\text{-}H}$	Other
(V)	Ph	Ph	6,6	1,75	
	OEt	Ph	8,5	1,75	
	OCH_2CH_2Br	Ph	9,5	1,75	
	SEt	Ph	10,1	1,75	
	SEt	Et	9,1	1,75	
(VII)	OEt	Ph	37,3	1,75	
(IXa)	OEt	OEt	34,0(34,5) *	1,75	7,1 † 0,6 ‡
	Ph	Ph	31,8(30,0) *	1,7	10,0 †
	OEt	Ph	29,6	1,85	7,5 † 0,5 ‡
	OCH_2CH_2Br	Ph	36,8	1,75	9,3 †
	OH	Ph	55,0	1,75	2,1 †
(IXb)	OEt	OEt	33,0	1,65	
	Ph	Ph	30,0	1,65	
	SEt	Et	30,0	1,75	
	OEt	Ph	35,0 **	1,75	
	OCH_2CH_2Br	Ph	35,0 **	1,80	
(IXc)	OEt	Ph	35,0	1,75	

*The coupling constants calculated using Eq. (1) are given in parentheses.

†The coupling constants of the β-proton in (IXa).

‡The coupling constants of the hydroxyl proton in (IXa).

**Approximate values of the coupling constants at 20°C are given (see text).

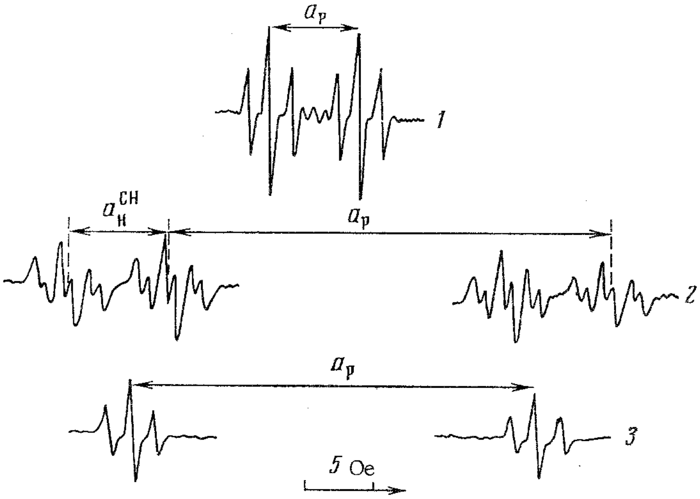


Fig. 1. ESR spectra of phosphorus-containing phenoxyl radicals: 1) radical (V) ($R^2 = R^3 = Ph$); 2) radical (IXa) ($R^2 = R^3 = OEt$); 3) radical (IXb) ($R^2 = R^3 = Ph$).

labile P–H bond would lead to the formation of the corresponding phosphorus-substituted phenols (IV), (VI), and (VIII). The oxidation of these phenols using PbO_2 should lead to the corresponding phenoxyl radicals (V), (VII), (IXa), (IXb), and (IXc).

Indeed, upon heating solutions of (I), (II), and (III) in diethyl ether in a sealed ampul in the presence of a phosphoryl hydride with subsequent treatment of the reaction mixture with PbO_2, we recorded ESR spectra corresponding to the formation of radicals (V), (VII), and (IX), whose parameters are given in Table 1. The ESR spectra of the three types of radicals (V), (VII), and (IX) show coupling of the unpaired electron with the ^{31}P nucleus

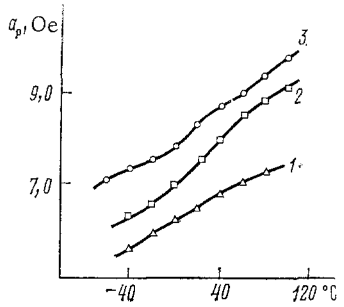


Fig. 2. Temperature dependence of a_P for radicals (V): 1) $R^2 = R^3 = Ph$; 2) $R^2 = OEt$, $R^3 = Ph$; 3) $R^2 = OCH_2CH_2Br$, $R^3 = Ph$.

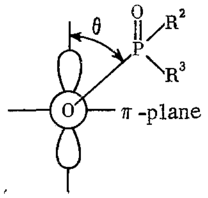
and protons of the phenoxyl ring (see Table 1, Fig. 1), confirming the proposed structure for these radicals. The coupling constants for (V) ($R^2 = R^3 = Ph$) were the same as those reported earlier [4].

Before describing the spectra of these radicals, let us examine the mechanism for coupling in the ^{31}P nuclei. The unpaired electron in the phenoxyl radicals is delocalized in the aromatic ring and the maximum spin density is found in the position para to the monovalent oxygen atom, i.e., in the position attached to the phosphorus-containing substituent. Thus, we should consider the coupling of the unpaired electron on the carbon atom in the β position relative to the phosphorus atom with the phosphorus nucleus. In this case, the coupling of the unpaired electron with the ^{31}P nucleus may depend significantly on the geometry of the radicals.

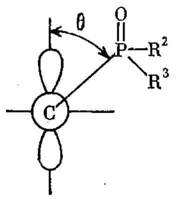
It is generally assumed that coupling in the ^{31}P nucleus is the result of a hyperconjugation mechanism and this coupling (a_P) depends on the nature of the substituents and temperature. The temperature dependence is related to the angular dependence of the coupling constant a_P which is given by the expression

$$a_P{}^{\beta} = \rho_C{}^{\pi}(B_0{}^P + B_2{}^P \langle \cos^2 \theta \rangle) \qquad (1)$$

where $B_0{}^P$ and $B_2{}^P$ are constants, $\rho_C{}^{\pi}$ is the spin density in the phenoxyl para position, and θ is the angle between the direction of the p orbital of the unpaired electron in the phenoxyl para position and the X–P bond, where X = O and C [5].



Type V radicals



Type IX radicals

Table 1 shows that the ^{31}P coupling in type V radicals is realtively low (θ ≈ 90°). We can only say the a_P increases with increasing temperature (Fig. 2).

Study of the temperature dependences of the ESR spectra of 4-hydroxyphenoxyl, 2,6-dimethyl-4-hydroxyphenoxyl, and 2,6-dimethyl-4-methoxyphenoxyl showed that the barriers to rotation of the OH and CH_3O groups about the C–O bond are 8-10 kcal/mole [6], while rotation ceases at −70°C on the ESR time scale: A nonequivalence is found under these conditions for the coupling constants of the ring protons and protons of the methyl groups at C-2 and C-6 of the corresponding radicals. The high barriers and low rotation frequencies ($\sim 10^7$ sec^{-1}) of the OH and CH_3O groups in the phenoxyls relative to the analogous parameters in diamagnetic compounds (for example, the barrier in anisole is 1.5 kcal/mole) is usually explained by double bond nature of the C–O bond in the >Ċ–OR fragment.

Hence, the rotation of the phosphorus-containing fragment in type V radicals is strongly hindered.

The absence of "indicator" nuclei such as in the above hydroxy- and methoxy-substituted phenoxyl radicals (ring protons and protons of the methyl groups at C-2 and C-6) does not

TABLE 2. Calculated Angles between the p Orbital of the Unpaired Electron and C—H (θ_{CH}), C—P (θ_{CP}), and C—O (θ_{CO}) Bonds in the IXa Radical

R^2	R^3	$\theta°_{CH}$	$\theta°_{CP}$	$\theta°_{CO}$
OEt	OEt	55	65	5(0,6) *
Ph	Ph	48,5	71,5	11,5(0)
Ph	OEt	52,7	67,3	7,3(0,5)
Ph	OCH_2CH_2Br	47	73	13(0)
Ph	OH	77,5	42,5	17,5(0)

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*The coupling constants (Oe) with the hydroxyl protons of the para substituent are shown in parentheses.

TABLE 3. Temperature Coefficients of the Coupling Constants a_H^{CH} and a_P in Radical IXa*

R^2	R^3	$d\bar{a}_H/dT$	$d\bar{a}_P/dT$
OEt	OEt	~0	−16,7
Ph	Ph	+8,3	~0
OEt	Ph	~0	~0
OCH_2CH_2Br	Ph	~0	−12,5

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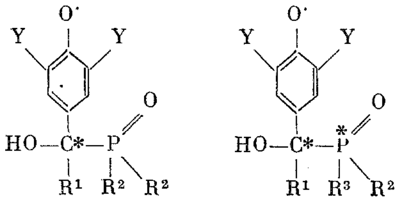
*A positive sign of the coefficient indicates an increase in the coupling constant with increasing temperature and a negative sign indicates a decrease.

permit us to estimate the kinetic parameters for rotation of the phosphorus-containing fragment in radicals (V). We can only say that radicals (V) exist at least in two equivalent equilibrium conformations with the same a_P and θ; the variation of a_P with temperature indicates that θ lies between 45 and 90°. This is related to the nonlinear nature of Eq. (1) upon torsional vibrations of the phosphorus-containing fragment relative to the C—O bond in the equilibrium conformations with angle θ. If the equilibrium conformations of radicals (V) were nonequivalent, different ^{31}P coupling constants would be observed at low temperatures with the cessation of rotation. However, this behavior is not observed experimentally.

In the case of type VII radicals, the value of a_P decreases from 38 to 37 Oe in the range from −80 to +40°C. Such a slight change in a_P for radicals (VII) indicates significant steric hindrance to rotation of the phosphorus-containing fragment about the C—C bond. The decrease in a_P with increasing temperature indicates that θ lies in the range from 0 to 45°, which is also supported by the significant value of a_P.

In preparing type VII radicals, the ESR spectra of the reaction mixture also shows strong signals for 2,6-di-tert-butyl-4-diphenylmethylphenoxyl ($a_{m\text{-}H}$ = 1.8, a_H^{CH} = 8.2 Oe) formed in the oxidation of the corresponding phenol. The initial phenol may arise in the reduction of methylenequinone (II) by phosphoryl hydrides, which apparently competes with the addition process.

Radicals (V) and (VII) obtained using different phosphoryl hydrides contain only one asymmetric center (the phosphorus atom). Type IX radicals have either one asymmetric center (carbon atom) or two such centers (carbon and phosphorus atoms).



$R^1 = H$ (IXa), CH_3 (IXb), CH_2COCH_3 (IXc).

Let us first examine the spectra of radical IXa since the ESR spectra of this species shows that the unpaired electron is coupled not only with the ^{31}P and phenoxyl ring meta proton nuclei but also with the CH protons of the substituent (a_H^{CH} is in the range from 6 to 10 Oe). The a_H^{CH} coupling constant is very sensitive to change in the orientation of the C—H bond relative to the p orbital of the unpaired electron in the phenoxyl para position. A quantitative theory for describing the coupling of the proton β to the carbon atom bearing the unpaired electron was developed in detail by Horstield et al. [7]. In the free rotation range, a_H^{CH} = 25 Oe and in the absence of free rotation, this term is given by the equation

$$a_H^{CH} = \rho_C^{\pi}(B_0^H + B_2^H \langle\cos^2\theta\rangle) \qquad (2)$$

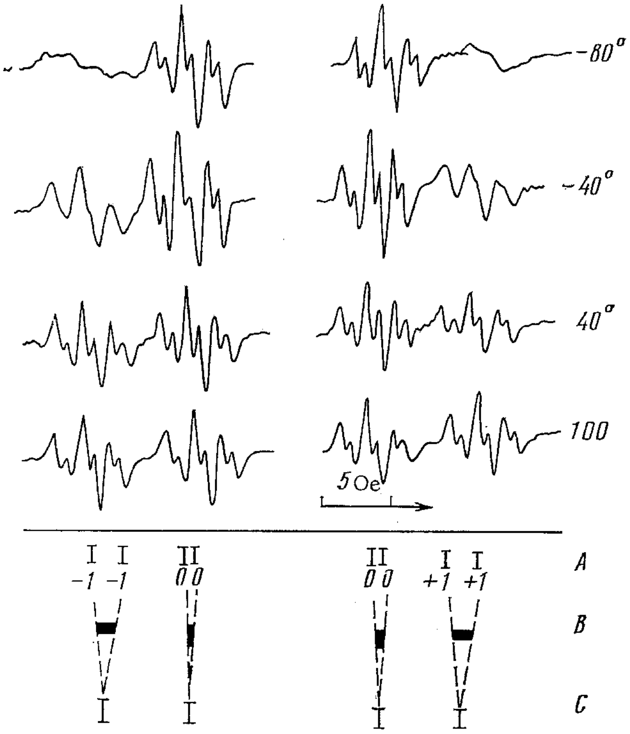
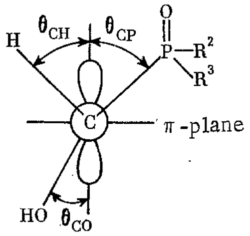


Fig. 3. Temperature changes in the ESR spectra of radicals (IXa) for $R^2 = R^3 =$ OEt. A scheme is given below for line broadening with change in a_P and a_H^{CH} in the same direction due to rapid vibrations of the para substituent relative to the C–C bond. A) slow exchange; B) intermediate exchange; C) rapid exchange.

The constants $B_0^H = 3.2$ Oe, $B_2^H = 43.5$ Oe [7] and ρ_C^π is the spin density which, in our case, is given by the spin density in the phenoxyl para position (∿0.4 [6]). Equation (2) permits us to estimate the angles in radical (IXa). Table 2 shows the angles between the C–H bond and the p orbital of the unpaired electron (θ_{CP})



Coupling of the hydroxyl proton is seen only at low θ_{CO}.

Study of the temperature dependence of the ESR spectra of radical (IXa) showed a significant change in a_P and a_H^{CH} in the range from –100 to +100°C. The temperature coefficients given in Table 3 for a_C^{CH} and a_P in the form of first derivatives of these terms relative to temperature indicate the lack of free rotation of the para substituent about the C–C bond. We may assume only torsional vibrations in the equilibrium conformations take place at high frequency (above the characteristic ESR time) while the frequency for the transition between these conformations is significantly lower. This conclusion is also supported by the significant change in the a_C^{CH} coupling constants in the 4-R-substituted 2,6-di-tert-butylphenoxyl radicals such as $a_H^{CH} = 10.7$ Oe for R = CH_3, $a_H^{CH} = 8.6$ Oe for R = C_2H_5, and $a_H^{CH} = 4.6$ Oe for R = C_6H_{11}.

Reversible broadening of the terminal spectral components was found for (IXa) radicals with $R^2 = R^3 =$ OEt or Ph (Fig. 3). The scheme at the bottom of Fig. 3 shows that the broadening of the terminal spectral components may be the result only of change of the a_P

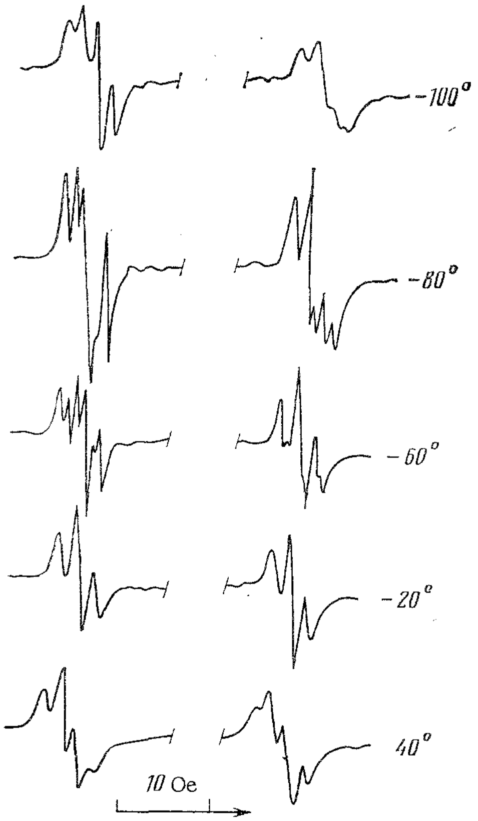


Fig. 4. Temperature changes in the ESR spectra of radical (IXb) with R^2 = OEt and R^3 = Ph.

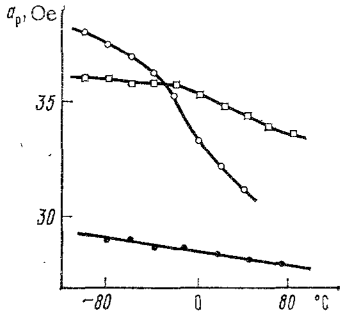
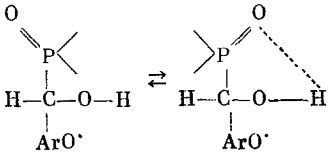


Fig. 5. Temperature dependence of the coupling constants of stereoisomers of radical (IXb) (R^2 = OEt, R^3 = Ph). The lower line corresponds to the analogous dependence for radical (IXb) with $R^2 = R^3$ = Ph.

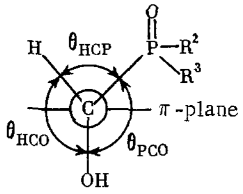
and a_H^{CH} constants in the same direction. Then, the distance between the exchanging lines (lines with the same projections of total nuclear spin) for the outer pair of lines will be greater than for the inner pair. Such a temperature pattern of the spectral behavior may be related to a change in the rate of transition between the equilibrium conformations comparable to the characteristic ESR time. However, in accord with the values found for θ_{CH} and θ_{CP}, such a transition should be accompanied by change in a_H^{CH} and a_P in opposite directions. Thus, in the case of cessation of the transition between conformations with decreasing temperature, the inner line pair should broaden. This behavior was not observed experimentally.

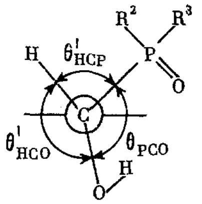
The same direction for change in a_H^{CH} and a_P and, thus, of θ_{CP} and θ_{CH} may be explained taking account of rotation of the phosphoryl substituent relative to the C—P bond. We should note that such a rotation may be accompanied by the formation of hydrogen bond between the hydroxyl hydrogen and oxygen atom of the phosphoryl group



where ArO˙ is the phenoxyl fragment in (IXa).

The formation of such hydrogen bonds was subjected to a detailed IR spectroscopic study for systems with phosphinyl-α-hydroxyalkyl groups, whose geometry permits the formation of a five-membered ring with an intramolecular hydrogen bond [8]. The formation of an intramolecular hydrogen bond in radicals (IXa) may alter the geometry of the para substituent, leading to distortion of the HCP, HCO, and PCO angles.





The prime sign (θ') indicates angles after formation of a hydrogen bond. Apparently, $\theta'_{HCP} > \theta_{HCP}$, $\theta'_{CHO} > \theta_{HCO}$, and $\theta'_{PCO} > \theta_{PCO}$.

The change in θ_{HCP} in the equilibrium conformation of radical (IXa) apparently leads to change in angles θ_{CP} and θ_{CH} and constants a_H^{CH} and a_P in the same direction. Thus, the line broadening found in the ESR spectra of radicals (IXa) may be caused by modulation of the equilibrium angles θ_{CP} and θ_{CH} due to rotation of the phosphoryl group relative to the C—P bond. Analysis of the observed broadening permitted estimation of the energy barrier of this process, E_a = 1.6 kcal/mole, which was close to that found in our previous work [8] (∿1 kcal/mole).

The values for θ_{CP} and θ_{CH} in radicals (IXa) permit estimation of B_0^P and B_2^P in Eq. (1). For greater accuracy in determining these parameters, we used the spectral data for (IXa) with R^2 = Ph, R^3 = OEt and R^2 = Ph, R^3 = OH (see Tables 1 and 2), in which the coupling constants have their greatest difference. Comparing the two equations taking account of the values found for $_{CP}$ employing Eq. (1), we obtain B_0^P = 62 and B_2^P = 136 Oe. To check the parameters calculated values, we calculated the a_P constants for (IXa) with $R^2 = R^3$ = OEt or Ph. The values obtained for B_0^P and B_2^P are in satisfactory accord with the calculated and experimental values of a_P (see Table 1). The coupling constants were taken at the lowest temperatures at which the torsional vibrations of the para substituent are minimal.

The significant value of B_0^P obtained in this work indicates that for θ_{CP} = 90° ("freezing" of the hyperconjugation mechanism), the significant ^{31}P coupling arises due to polarization of the σ bonds and multielectron cloud of the phosphorus atom and the large isotropic coupling calculated for the phosphorus atom (a_P^{iso} = 3640 Oe) [9] relative to that calculated for the hydrogen atom (a_H^{iso} = 500 Oe) [10].

The ESR spectra of radicals (V), (VII), and (IXa) and the temperature effect on these spectra only indicate the lack of free rotation of the phosphorus-containing substituents relative to the C—O and C—C bonds. The ESR spectra of radicals (IXb) and (IXc) which contain two asymmetric centers clearly show a diastereomeric effect leading to two ESR spectra with different a_P constants corresponding to two diastereomers. Spectrum 3 in Fig. 1 shows the ESR spectra of (IXb) radicals with identical substituents $R^2 = R^3$ = OEt or Ph which have one coupling with ^{31}P nuclei such that the diastereomeric effect is absent. Figure 4 shows ESR spectra of radicals (IXb) with different substituent R^2 = OEt, R^3 = Ph or R^2 = CH_2CH_2Br, R^3 = Ph which display two ^{31}P coupling constants. The a_P values of the spectrally distinguishable stereoisomers differ considerably from one another with change in temperature (Fig. 5). The relative intensity of the two forms, which correspond to different ^{31}P coupling constants, are independent of temperature. This independence is convincing support for the existence of a diastereomeric effect in radicals (IXb). Analogous spectral behavior is also observed for radicals (IXc).

EXPERIMENTAL

All the radicals studied were obtained by brief but intense heating (at ∿150°C) of solutions of the starting compounds in ampuls in the presence of phosphoryl hydride compounds. After opening and the addition of PbO_2, the ampuls were evacuated, heated slightly, and placed in the probe of a Varian E-12A ESR spectrometer. In addition to the phosphorus-containing radicals, ESR spectra were almost always recorded for radicals of the starting phenol (III) on account of incompleteness of the reaction. The best results were obtained upon heating the starting compounds without solvent with subsequent dissolution of the reaction products.

The thio esters of the phosphonous acids, which are unstable under ordinary conditions, were obtained by hydrolysis of the corresponding acid chlorides directly in the reaction mixture by the addition of small amounts of water.

CONCLUSIONS

1. The reaction of sterically hindered p-hydroxycarbonyl compounds with organophosphorus compounds with labile P—H bonds leads to the formation of phosphorus-containing sterically hindered phenols whose oxidation leads to the formation of relatively stable phenoxyl radicals.

2. A diastereomeric effect is seen in the ESR spectra when the radicals have two asymmetric centers.

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