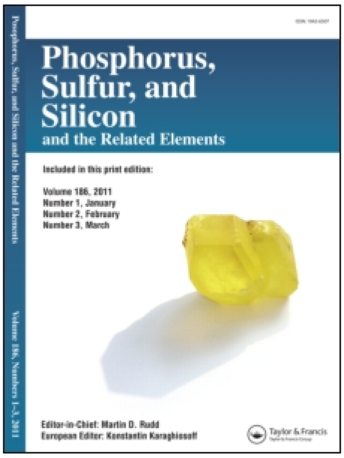

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CHARGE TRANSFER REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS WITH *P*-QUINONES

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CHARGE TRANSFER REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS WITH *P*-QUINONES

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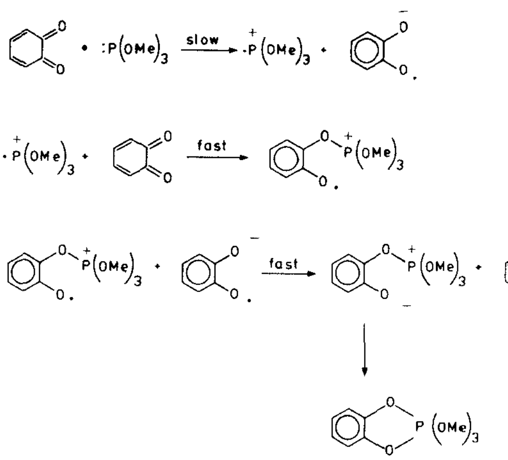
Reactions of trivalent phosphorus compounds with suitable aromatic acceptor molecules proceed via a radical mechanism. In the case of *p*-quinones, the products and intermediates are identified by esr and an appropriate mechanism is outlined. The esr-data of the radicals are interpreted by means of spin density calculations.

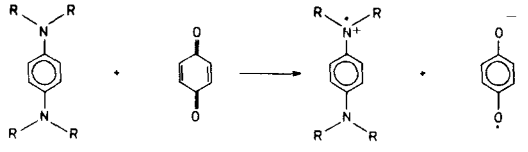
INTRODUCTION

It is well-known that trivalent phosphorus compounds easily react with *o*-quinones or α-diketones.[1b] The mechanism of these condensations involves the generation of a phosphinium radical by a one-electron transfer from the phosphorus compound to the carbonyl compound,[1a] e.g.:



SCHEME I

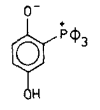
It seems reasonable that the first step in this reaction sequence may be applied to other electron acceptors like *p*-quinones. However, the same type of condensation product cannot be formed, due to the separation of the oxygen atoms. Similar reactions with *p*-phenylene-diamines lead to the stable Würster salts, which are in fact combinations of a radical cation and a radical anion:



The stability of the phosphinium ion is expected to be less than that of the radical cation mentioned above. This is demonstrated by a similar color as in the preparation of the Würster salts, which appear *only* in the early stages of the reaction with aromatic phosphines, e.g. triphenylphosphine.

The final product of this reaction is proved[3] to be compound **1**, so the strong electrophilic phosphinium cation radical may be concluded to have attacked the aromatic system, followed by a proton transfer to an oxygen atom and reduction.

Using trimethylphosphite, however, a different compound (**2**) is formed, according to Ramirez:[1b]



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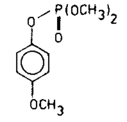

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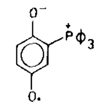

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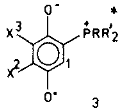
The esr-spectrum showed the presence of a species with the phosphorus atom attached to the *ring*, like compound **1**. So, the phosphinium radical has the opportunity of attacking on two sites of the *p*-quinone molecule and two products are formed.

Strong evidence is available that the formation of the methyl ether of *p*-quinoldimethyl phosphate (**2**)

TABLE I



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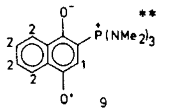

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Solvent	R	R'	X	a_P	a_1	a_2	a_3	a_N	Ref.
C_6H_6	NMe_2	NMe_2	H	4.53	5.05	1.57	1.57	0.23	*
CH_2Cl_2	Ph	NMe_2	H	4.00	5.55	1.55	1.55	≃ 0.3	2 *
CH_2Cl_2	NMe_2	NMe_2	CN	2.5	3.2	0.4	0.4	< 0.2	*
C_6H_6	Ph	Ph	H	4.42	5.35	1.4	1.4		*
CH_2Cl_2	Bu	Bu	H	4.70	5.15	1.70	1.70		2 *
CH_2Cl_2				5.78	6.72	0.57		0.40	**

takes place by means of a radical mechanism (see Discussion).

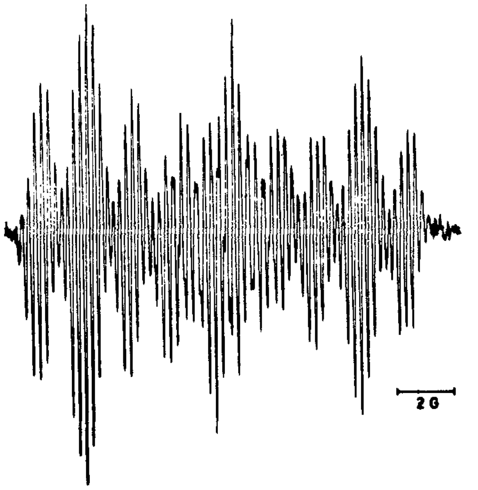


FIGURE 1 Esr spectrum of the radical adduct of *p*-benzoquinone and TDAP in benzene (type 3).

RESULTS

A Reactions of p-Benzoquinones

When equimolar amounts of *p*-benzoquinone and triphenylphosphine in benzene are mixed, an orange-red colour develops and a yellow solid slowly precipitates in quantitative yield. The reaction can be followed in the cavity of the esr-apparatus and a signal of strong intensity was detected as long as the orange colour was visible. The yellow precipitate has according to experiments of Ramirez[3] structure **1**. This experiment suggests that an orange-red radical could be the reaction intermediate. The spectral data of this radical (Table I) can be best interpreted in terms of structure **3**. However, using trimethylphosphite or triethylphosphite no precipitate was observed, although about the same colour in combination with a paramagnetic solution was observed. Nmr measurements indicated that compound **2** was mainly formed ($\delta_{OCH_3} = 3.77$ ppm; $\delta_{P(OCH_3)_2} = 3.83$ ppm; $\delta_{Phenyl} = 6.87$ and 7.17 ppm; $J_P = 11.7$ Hz; $J_{Phenyl} = 9.8$ Hz).

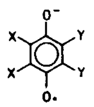
These observations indicate that two reactions may occur.

If the same reaction was carried out in the presence of the scavenger 2-methyl-2-nitrosopropane, the esr spectrum showed the presence of trapped methyl radicals ($a_N = 15.7$ G and $a_{CH_3} = 11.6$ G).

During the reaction of *p*-benzoquinone with tris(dimethylamino)phosphine (TDAP) the orange colour darkened after a few minutes and no solid was formed, though a strong esr signal was observed. However, during the recording of the spectrum the signal intensity decreased quickly (see Figure 1). This is an indication that the radicals formed during the reaction are unstable. For this reason no pmr spectrum of the products could be obtained either. The esr spectrum was similar to the one obtained by the reaction with trimethylphosphite interpreted in terms of radical type **3**.

B The Reaction of 2,3-Dicyanodichloro-p-benzoquinone (DDQ) with TDAP

No remarkable colour was observed during this reaction, but a very strong signal of quinone anion radical **4** with additional ^{13}C lines appeared ($a_N = 0.59$ G, $a_C = 2.42$ and 2.86 G). Besides, a less intense doublet with a splitting constant of 7.53 G was visible. This observation differed from earlier observation where the phosphorus splitting constants were smaller. The phosphorus atom cannot be attached to the substituted phenyl ring, so the measured radical is probably **5**.



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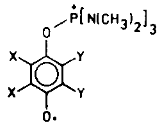
X = H or Cl
Y = CN



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As can be seen in Figure 2 the spectrum shows a hyperfine structure, due to the five nitrogen atoms. The coupling constant seems to be equal for the two groups of nuclei (0.49 G). This value is in good agreement with the a_N's of radicals **4** and dimethylamino-substituted **3** (0.59 and 0.24 G, respectively).

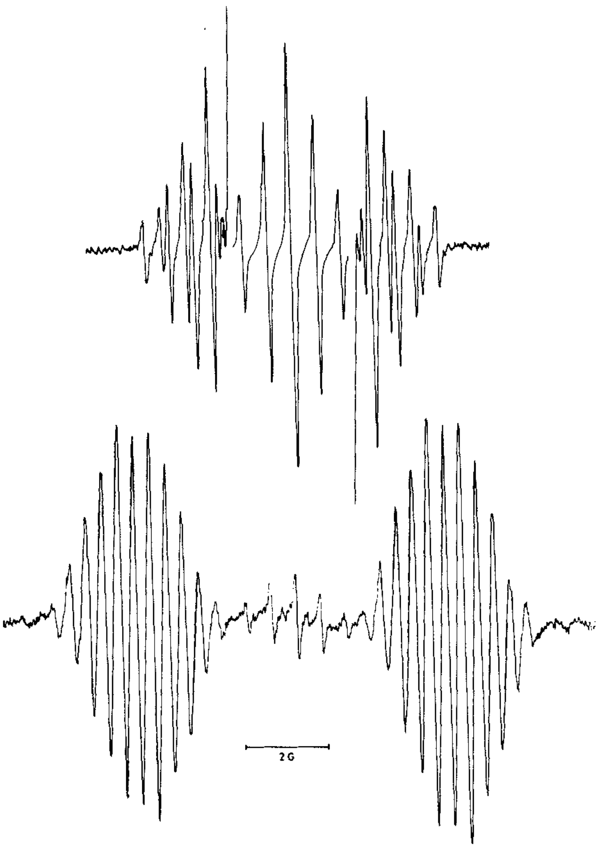
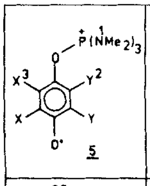
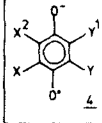


FIGURE 2 Esr spectra of the DDQ anion radical (above) and the adduct radical of DDQ and TDAP (below) in benzene.

C The Reaction of 2,3-Dicyano-p-benzoquinone with TDAP

In this quinone two sites can be attacked by a phosphinium radical, i.e. on the phenyl ring or on the oxygen atom. The esr spectrum shows a doublet of 10.61 G, so radical type **5** is probably formed. In some experiments, however, where an excess of the quinone was used, an unstable radical of type **3** (two doublets of quintets) was measured ($a_H \simeq a_P = 3$ G).

TABLE II

	X	Y	Solvent	a_P	a_1	a_2	a_3
 5	Cl	Cl	C_6H_6	2.28	<0.8		
	Cl	CN	C_6H_6	7.53	0.49	0.49	
	H	CN	C_6H_6	10.61	0.36	1.08	1.80
	H	CN	C_6H_6/ CH_2Cl_2	10.75	0.42	1.19	1.95
 4	H	H	C_6H_6		2.36	2.36	
	H	CN	DME		0.66	1.09	
	Cl	CN	C_6H_6		0.59		

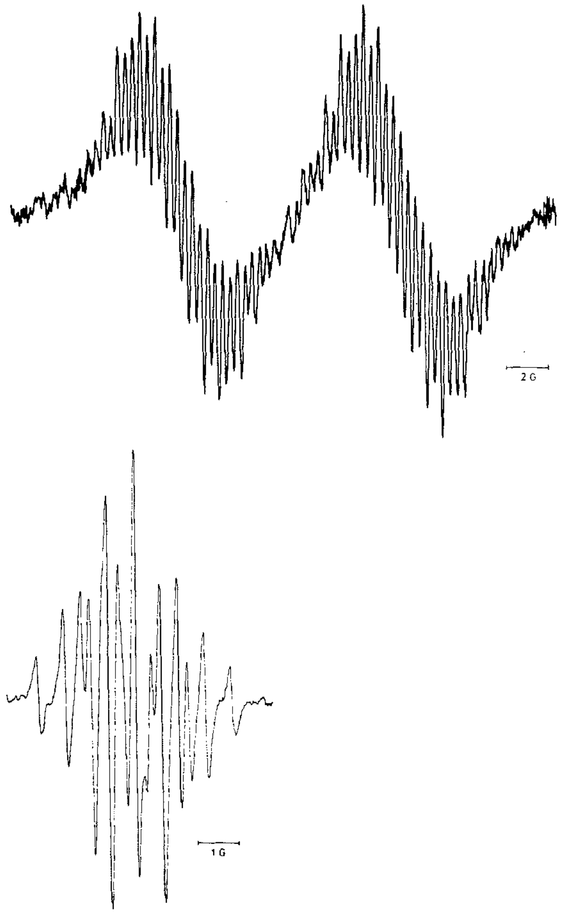


FIGURE 3 Esr spectra of 2,3-dicyano-*p*-benzoquinone anion radical in DME (left) and the adduct radical (5) of the quinone with TDAP in benzene.

The stable radical has an additional fine structure of five nitrogen and two hydrogen atoms of which the coupling constants are solvent-dependent.

During this reaction no *p*-quinone anion radical was detected. The spectrum of this radical was obtained by electrolysis in dimethoxyethane and the spectral data are given in Table II. Although additional ^{13}C-lines were visible, the intensity of the signal was too weak to obtain the correct hfs constants.

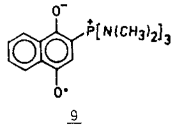
Finally, reaction of both cyano-substituted quinones with trialkylphosphites did not give a paramagnetic solution, which is to be explained in the Discussion.

D Reactions of Chloranil

The reactions of tetrachloro-*p*-benzoquinone-(chloranil) with TDAP and trimethylphosphite gave rise to the formation of radicals of which the esr spectra show the following features: a small phosphorus hfs constant (2.28 G and 2.42 G, respectively) and a large line width. The radicals must reasonably be of type **4** and several authors[3,4] have suggested this structure in the reaction of chloranil with other phosphines or phosphites. However, on theoretical grounds a hfs constant of approximately 20 G is expected.

E Reaction of 1,4-Naphthoquinone with TDAP

An esr signal of high intensity was measured in this case due to the formation of a radical of type **3** possessing the following structure:



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The hfs constants of this radical are given in Table I and are comparable to the data given by Lucken[2] in which other phosphines were used.

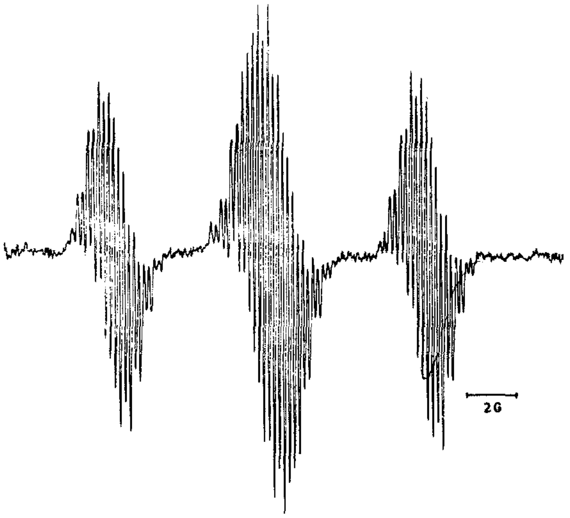
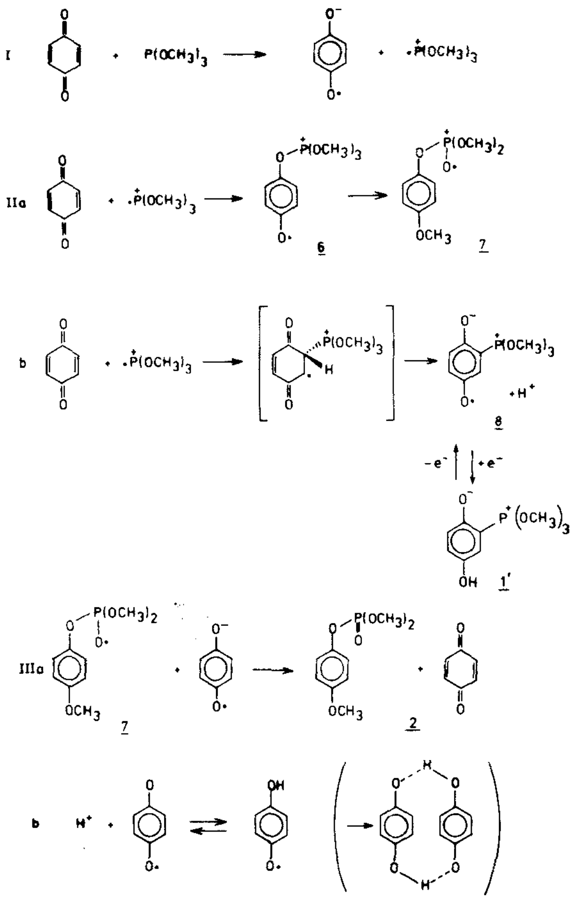


FIGURE 4 Esr spectrum of the adduct radical of TDAP with 1,4-naphthoquinone in benzene.

DISCUSSION

It is obvious that the reaction sequence mentioned in the Introduction applies to reactions of trivalent phosphorus compounds with *p*-quinones: highly reactive phosphinium radicals are formed and addition takes place with neutral quinone molecules (Scheme II).



SCHEME II

A new aspect is the availability of a second active site in *p*-quinones, i.e. the phenyl ring. Substitution of an aromatic proton is involved here, resulting in the formation of a free "Zwitterionic" radical.

In the pmr spectrum the methyl ether of *p*-quinoldimethylphosphate (**1'**) was observed exclusively, while in the esr spectra radical **8** and sometimes the quinone anion radical were recorded. It is suggested that reactions IIb and IIIb are reduction-oxidation equilibria involving **8** and monohydroquinone free radical (chinhydron), stabilized by the apolar solvent benzene. In some reactions a concentration of the quinone anion radical was built up if the rate of the main reaction was too low, i.e. when less than equimolar amounts of quinone were used.

Using TDAP, a rearrangement of the adduct radical is impossible (e.g. the conversion from **6** into **7**) and a tarry degradation product is observed next to a radical of type **8**. It is not surprising that the stability of this radical is low in benzene.

If the phenyl ring of the quinone is substituted by atoms other than hydrogen atoms, the formation of type **8** radicals is unlikely. In the reaction of DDQ with TDAP the recorded esr spectrum is of radical type **6**. Although step I is favoured with respect to the reaction with the unsubstituted quinone, the intensity of the signal is inferior to the one described above. If the radical is able to isomerize (DDQ with trimethylphosphite) to **7**, no radicals were observed.

ESR SPECTRA AND SPIN DENSITY CALCULATIONS

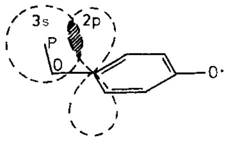
Three different types of radicals are described in this section, viz. quinone anion radicals (**4**), phosphoranyl radicals (**3**) and β-phosphorus-substituted radicals (**5**, **6**). For the calculation of spin densities in type **3** and **4** the following formula can be applied[16]:

$$a^{X} = \left(S^{X} + \sum_{i} Q^{X}_{XY_i}\right)\rho_{X} + \sum_{i} Q^{X}_{Y_iX}\rho_{Y_i}$$

S^X covers the polarization of 1*s* electrons and the Q^X_{XY} and Q^X_{YX} terms represent spin polarization in the X—Y σ-bonds from spin densities on the atom under consideration and on neighbouring atoms. *S* and *Q* parameters are given by Fraenkel and coworkers[5–7] with respect to carbon, oxygen and nitrogen. For phosphorus a value of 80 G is derived with respect to the expression $(S^P + \sum_i Q^P_{Pi})$ from the observed ^{31}P hfs constant of $\dot{P}H_2$.[8] In this radical the odd electron resides in a p_z-orbital on phosphorus and a positive sign is indicated.[9] The adjacent atom term Q^P_{YP} is set on value of 40 G for Y being a carbon atom and 33 G for Y being an oxygen atom according to the experimental a_P's in the radicals $H_2\dot{C}—\overset{+}{P}Ph_3$[10] and $\dot{P}O_4^{2-}$[11] respectively. From the point of view that spin polarization induces a negative spin density on the atoms linked to the radical centre, a negative sign must be indicated.

However, for radicals of type **6** the phenomenon of hyperconjugation prevents a proper calculation with respect to the phosphorus hfs constant.

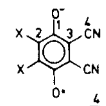
In general, this contribution to the splitting constant is approximately equal to: $a^X = (B_0 + B_2\cos^2\theta)\rho_\pi$. B_0 is small and can be neglected, B_2 is 56–60 G for alkyl radicals and approximately 20–30 G for the kind of phosphorus radicals described here according to the radical with the largest phosphorus hfs constant.[12] θ is the dihedral angle between the O—P bond and the axis of the p_z orbital associated with the aromatic system:



6

It can easily be seen that introduction of bulky groups ortho to the P—O group leads to a preference for a conformation in which the phosphorus atom is out of the plane of the aromatic ring ($\theta = 0$) providing maximum overlap between the carbon p_z and phosphorus 3*s*-orbitals.

TABLE III



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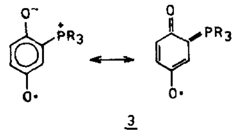
Mode	X	a_N	a_X	a_{C_1}	a_{C_2}	a_{C_3}	a_{C_4}
exp.	Cl	0.59		-2.86		2.42	
calc.(INDO)	F	0.30	0.05	-5.48	0.60	2.92	-1.81
exp.	H	0.66	1.09				
calc.(HMO)	H	0.43	2.06	-0.98	0.61	-0.15	-2.07

A QUINONE ANION RADICALS

During most of the reactions quinone anion radicals were observed according to the first step of the reaction. The most interesting ones are the dicyano-substituted radicals. The DDQ anion radical was present in such a high concentration that ^{13}C-lines were visible (see Discussion and Figure 2). This spectrum is measured by Kolodny and Bowers[13] too, although they ascribed the ^{13}C-lines to a charge transfer complex radical of DDQ and *p*-phenylenediamine. Regarding the electrolytically generated dicyano-*p*-benzoquinone anion radical, no ^{13}C-lines could be observed and for this radical spin density calculations are performed. To obtain the correct coefficients of the singly occupied orbital the following parameters are used: $\delta_O = 1.6$; $\delta_N = 1.0$; $\gamma_O = 1.2$ and $\gamma_N = 2.0$, according to Rieger and Fraenkel.[7] Using the formula mentioned earlier in this section hfs constants for this radical are calculated. For the DDQ anion radical a_N equals 0.49 G which is in proper agreement with the other values and the two carbon hfs constants may be ascribed to the cyano carbon atom and to the atom attached to chlorine.

B Phosphoranyl Radicals

In these radicals a tetrahedrally coordinated phosphorus atom (positively charged) is linked to a radical anion (**3**). Tso-electronic radicals in a trigonal bipyramid possess high phosphorus splitting constants (700–1300 g). However, when the odd electron is able to delocalize to the phenyl ring, the splitting constants are in the range of 5–20 g.[14] Here, these radicals are products of reaction I and IIb, according to the mechanism in Scheme II. These radicals are resonance-stabilized as follows:



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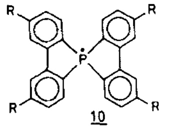


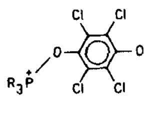
10

The phosphorus hfs constants are in the range of 4.5–6.5 G for monoarylsubstituted radicals and 10–20 G for symmetric bis(biphenylene)-substituted radicals **10** according to Rothuis.[15] In the latter *all* carbon atoms attached to phosphorus possess a certain spin density which accounts for slightly larger a_{P}'s. It should be noted that the radical generated during the reaction of triphenylphosphine and *p*-benzoquinone must be described as a monoaryl-substituted radical, while no spin density was observed in the three phenyl rings. Rothuis described a similar radical (**10**, substituted with *one* nitro group, $a_{\mathrm{P}} = 6.5$ G). The similarity between the two species is an electron-withdrawing group.

The observed small a_{P}'s are due to a π-spin density both on the phosphorus atom and the adjacent carbon atom(s) for which the relation mentioned earlier is valid, using the appropriate values for the spin polarization constants (Q).

C β-Phosphorus-Substituted Radicals

The major contribution in the phosphorus hfs constant is of hyperconjugative character, although the contribution of spin polarization is not negligible (a certain spin density is measured for the nitrogen atoms attached to phosphorus, i.e. the reaction products of TDAP). Assuming hyperconjugation exclusively, the phosphorus hfs constant is dependent on the kind of substitution on the aromatic system. Its value (2–20 G) increases on introduction of steric restrictions which indicates that the a_{P} is favoured by conformations out of the plane of the aromatic ring.[12] However, introduction of chlorine as a substituent reduces the a_{P} as can be seen from the radicals generated during the reaction of TDAP with 2,3-dicyano-*p*-benzoquinone, DDQ and chloranil (10.61, 7.53 and 2.28 G, respectively).



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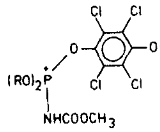

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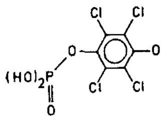

13

R = Ph or $N(CH_3)_2$

$a_{\mathrm{P}} \simeq 2.4$ G $\quad a_{\mathrm{P}} = 19.1$ G $\quad a_{\mathrm{P}} = 20$ G

This indicates that spin polarization (which gives a negative contribution to the a_{P} in contrary to hyperconjugation) becomes important in these radicals. A remarkable difference in the a_{P} is observed in radicals **11**, **12** and **13** which can be explained by assuming spin density on R with respect to radical **11**.

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