

Reactions of trivalent phosphorus compounds : an ESR study

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REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS

AN ESR STUDY
G. BOEKESTEIN



**REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS.
AN ESR STUDY**

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE
WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL EINDHOVEN, OP
GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. IR. G. VOSSERS,
VOOR EEN COMMISSIE AANGEWEEZEN DOOR HET COLLEGE VAN DEKANEN
IN HET OPENBAAR TE VERDEDIGEN OP DINSDAG 30 SEPTEMBER 1975
TE 16.00 UUR

door

GERRIT BOEKESTEIN
GEBOREN TE 'S-GRAVENZANDE

Dit proefschrift is goedgekeurd door
de promotoren
prof.dr.H.M.Buck
en
prof.dr.Th.J.de Boer

Aan mijn ouders

Mocht dit boek later ooit ontdekt worden, bij voorbeeld door iemand van de volgende generatie die de rommelige nalatenschap van zijn voorgangers uitzoekt, dan zal hij ongetwijfeld even glimlachen, want er zal nog veel gebeuren in de toekomst waar wij geen weet van kunnen hebben.

Olaf Stapledon

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CHAPTER I

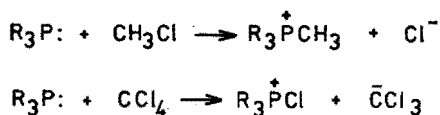
General introduction

I.1 Trivalent phosphorus compounds in relation to organophosphorus chemistry

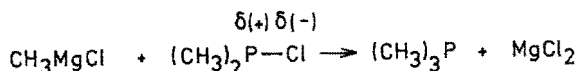
The chemistry of organophosphorus compounds has become an important issue in chemistry for the last ten years. The origin of this increased interest is of two kinds, *e.g.* the merous synthetical possibilities of trivalent phosphorus compounds, due to the ease of inclusion of the 3d-orbitals and the fact that particular phosphate esters (ATP) may control transfer of energy in living organisms.

Trivalent phosphorus compounds may be derived from phosphine (PH₃) and from phosphorous acid P(OH)₃ which is unstable and exists as phosphinic acid H₂PHO₃. The former are generally synthesized from PCl₃ by means of a Grignard reaction (*vide infra*) and are called phosphines. Phosphites are derived from phosphorous acid and may be obtained by esterification.

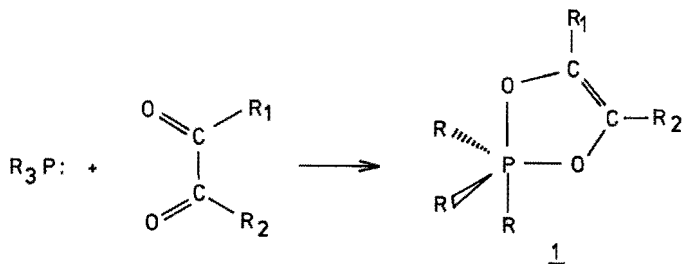
Trivalent phosphorus compounds are related to nitrogen compounds because of the similarity of the configuration of the outer-shell electrons. Both can expand easily their coordination number from three to four by "lending" their lone pair to electrophilic compounds. The addition of positively charged species is leading to phosphonium ions:



Both reactions are described extensively in the literature^{1,2}, the former with respect to its important application, *viz.* the Wittig reaction in order to synthesize various alkenes. However, substitution will occur if the trivalent phosphorus compounds themselves are acting as electrophilic reagents, *viz.* if the phosphorus atom is attached to a more electronegative atom such as chlorine:



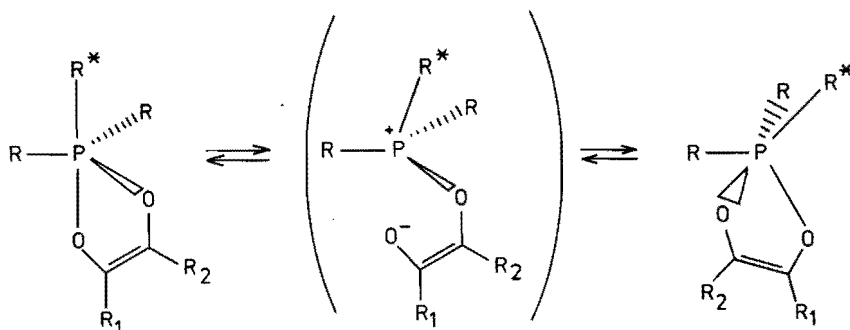
In contrast to nitrogen compounds, phosphorus compounds can extend their coordination number to five or even six. Pentavalent phosphorus compounds are commonly known and this means that phosphorus can accommodate 10 electrons in its outer-shell by utilizing its empty 3d-orbitals. So, trivalent phosphorus compounds are adding easily to unsaturated compounds, too, involving the rupture of a π -bond³:



The most stable configuration in compounds possessing a phosphorus atom with coordination number five is the trigonal bipyramidal one. Many compounds have been synthesized having a five-membered ring like dioxaphospholene 1 where one oxygen atom is in an apical (axial) position and the other one in an equatorial position.

These compounds may undergo stereoisomerization involving the permutation of the three substituents R which can be followed by means of NMR, because the apical and equatorial

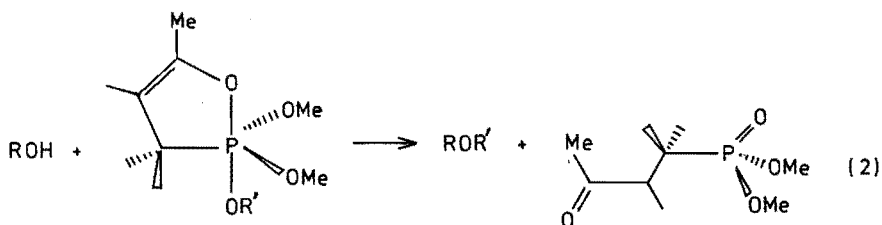
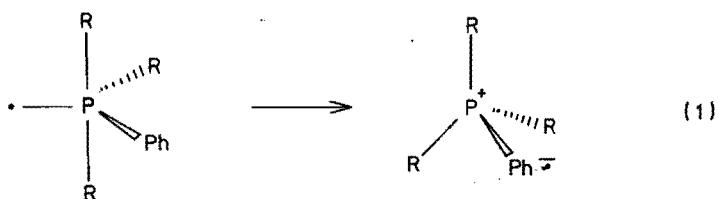
sites are not equivalent. If the isomerization is sufficiently fast on the NMR time-scale only one signal is measured and two signals otherwise. This process is called pseudorotation and two mechanisms are suggested. In the so-called Berry mechanism⁵, two apical and two equatorial substituents are changing simultaneously with one equatorial substituent as a pivot.



Pseudorotation according to this mechanism may be accompanied by cleavage of a P-O bond if R is an electron-donating group and R₁ or R₂ an electron-withdrawing group, *viz.* R=N(CH₃)₂ and R₁=COCH₃⁶. Examples of these dipolar tetrahedrally coordinated structures are given elsewhere in this thesis. However, the alternative mechanism provides the conservation of the OPO angle and this so-called turnstile mechanism must be followed in bicyclic pentavalent phosphorus compounds⁶. The ease of conversion of pentavalent phosphorus compounds to tetragonally coordinated structures may be illustrated by two other examples, *i.e.* stereoisomerization of phosphoranyl radicals (1) (1, see also Chapter V) and alkylation or acylation of carbon acids (2)⁷.

From the experiments described in this theses, additions towards trivalent phosphorus compounds do follow a radical mechanism which has been followed in several key reactions by means of Electron Spin Resonance (ESR). The first and rate-determining step is the electron transfer of the phosphorus compound to the compound to be added. Obviously, this is a

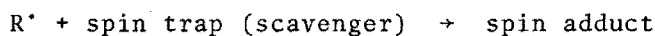
second-order reaction and strong electron-accepting molecules, which are called activated molecules, are reacting easily.



R=alkoxy; R'=alkyl or acyl

1.2 Spin Trapping

Spin trapping is a method to recognize unstable, short-lived radicals by adding them to an unsaturated function to produce a so-called spin adduct which is, in general, stable:

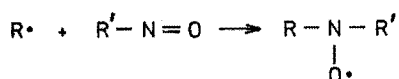
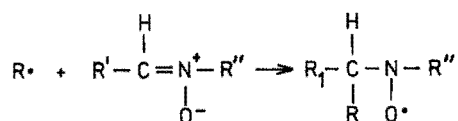


It appeared to be that compounds containing an NO-group are the most suitable to act as scavengers because of delocalization of the unpaired electron to the oxygen atom. Two important groups of such compounds are used in this field, *i.e.* nitrones (2), developed by *Janzen and Blackburn*⁸ and nitroso compounds (3), developed by *Mackor, de Boer and co-workers*⁹.

In both cases the spin adducts are called nitroxides and these compounds are also used in a strongly related technique, *i.e.* spin labeling. Here, those stable paramagnetic compounds are used to study diamagnetic systems, *e.g.* biolo-

gical macromolecules, whereas spin trapping is based on the use of diamagnetic molecules to study paramagnetic systems.

Another method of studying short-lived radicals is CIDN(A)P where the existence of two of those species at a close distance (in a "cage") causes nuclear magnetic resonance emission or enhanced absorption¹⁰.



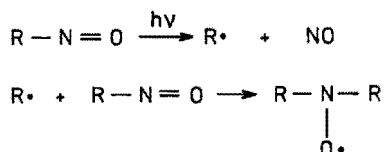
The experiments with respect to spin trapping as described in this thesis are mainly carried out with 2-methyl-2-nitrosopropane (or nitroso-t-butane) as the scavenger. The main advantages of nitroso compounds over nitrones are:

1. The multiplicity of the splitting pattern easily gives the number and nature of atoms in the α and β and in some cases the γ positions with respect to the nitrogen atom in the adduct radical.
2. The magnitude of the nitrogen hfs constant is a good indication for the nature of atoms which carried the odd electron in the trapped radical, *viz.* carbon¹¹ (13-16 G), phosphorus (10-12 G), oxygen¹² (27-28 G) and nitrogen (16-19 G).
3. Relatively small amounts of reactants yielding the short-lived radicals are sufficient to give a proper identification of the intermediates.

The disadvantages, however, are:

1. Some spin adducts are relatively unstable, since the added radical is directly linked to the nitroxide function and the possibility of a reverse reaction or some other cleavage reaction always exists.

2. Nitroso compounds do absorb radiation in the visible region yielding nitrogenmonoxide and the remaining paramagnetic fragment of the molecule is added to the unreacted scavenger.¹³



That is why most reactions concerning 2-methyl-2-nitrosopropane are carried out in the dark or at low temperatures.

Nitroso compounds usually exist in colourless trans-dimeric configurations which are in equilibrium with the coloured monomeric forms in solution. These equilibria are favoured to the side of the monomere in apolar solvents and *vice versa*.

Next to the use of 2-methyl-2-nitroso-propane the compound nitrosobenzene is used in some experiments, but analysis of the spectra of the adduct radicals was more difficult because of delocalization of the unpaired electron to the phenyl ring.

The compound 3,5-di-t-butyl-4-hydroxy-phenyl-t-butyl-nitron (4) was tried out in some experiments, too.¹⁴ This scavenger has the advantage of serving as a "bifunctional" spin trap in distinguishing carbon and oxygen centered radicals according to the scheme on next page.

However, experiments with scavengers 2 and 4 are not described in this thesis, for the spin trapping experiments are only carried out to recognize a limited number of short-lived radicals for which the use of 2-methyl-2-nitrosopropane is sufficient.

Although measurements with respect to the g-factor of spin adducts reveal supplemental information, they were not applied here, because experimental difficulties, *i.e.* the use of a standard such as DPPH^{*}, outweighed the advantages.

I.3 Scope of this thesis

A considerable number of reactions of trivalent phosphorus compounds are radical reactions due to the reducing action of these compounds. The most frequent types of reactions are investigated by means of Electron Spin Resonance (ESR). Where short-lived radicals are concerned the technique of spin trapping is applied. Furthermore, reactions of trivalent phosphorus compounds with photochemically generated radicals are studied, yielding phosphoranyl radicals.

Chapter II deals with the reaction of the strong electron-donating tris(dimethylamino)phosphine with activated (aromatic) bromides. Radical reactions are described in combination with the normal reaction route, *viz.* the formation of phosphonium salts, depending on the nature of the solvent. The formation of a stable dianion radical is described and proper reaction mechanisms are suggested to account for all the observations. Furthermore, spin density calculations with respect to the measured radicals are carried out for which the relatively simple Hückel MO-McLachlan procedure will give the best results. A description of this procedure is offered, too. Parts of this chapter were published in 1973¹³.

Chapter III emphasizes reactions with activated carbonyl compounds, *e.g.* aromatic diketones (with oxygen ortho-substituted) and aromatic aldehydes. A three-step radical mechanism is established here. It will be shown that this is more probable than the ionic mechanism as suggested by other authors. Side reactions concerning the transfer of alkyl radicals are described, revealing further evidence for the important role of trivalent phosphorus compounds in initiating radical reactions. The most essential information with respect to this subject was published in 1974¹⁴.

Chapter IV is concerned with reactions of PR_3 and para-quinones. The mechanism already mentioned in chapter II can be applied, but another site of the molecule can be attacked, too, as described by several authors before. The influence of substituents is discussed and several ESR spectra of interesting radicals are described. In one case ^{13}C -satellites are observed and the corresponding spin density calculations are offered.

In chapter V two stereoisomers of phosphoranyl radicals are described which are recognized easily from the magnitude of the ^{31}P hyperfine splitting (hfs) constant. These two types possess the tetragonal and the trigonal-bipyramidal configuration, respectively. The most important properties of these radicals are described and spin density calculations as well as calculations concerning the relative stability of the two types are offered, for which proper agreement has been achieved with the experimental results. Part of this work was published in a preliminary communication¹⁵.

Finally, in chapter VI experimental details are offered with respect to the instruments, computer programs and synthesis of the compounds used in this work.

References

1. Organophosphorus Chemistry, Vol. 1-5, The Chemical Society, London.
2. Organic Phosphorus Compounds, Vol. 1-7, John Wiley and Sons, New York.
- 3a. F. Ramirez, N.B. Desai and R.B. Mitra, J. Amer. Chem. Soc. 83, 492 (1961).
- b. V.A. Kukhtin, N.S. Garifyanov and K.M. Orekhora, J. Gen. Chem. USSR 31, 1070 (1961).
4. R.S. Berry, J. Chem. Phys. 32, 933 (1960).
5. F. Ramirez, Acc. Chem. Res. 1, 169 (1968).
6. F. Ramirez, I. Ugi, F. Lin, S. Pohl, P. Hoffman and D. Marquarding, Tetrahedron 30, 371 (1974).
7. W. Voncken and H.M. Buck, Rec. Trav. Chim. 93, 210 (1974).
8. E.G. Janzen and B.J. Blackburn, J. Amer. Chem. Soc. 91, 4481 (1969).
9. A. Mackor, Thesis Amsterdam (1968).
10. R. Kaptein, Thesis Leiden (1971).
11. E.G. Janzen, Acc. Chem. Res. 2, 279 (1969).
12. A. Mackor, Th.A.J.W. Wajer and Th.J. de Boer, Tetrahedron Lett. 1968, 1623.
13. Th.A.J.W. Wajer, A. Mackor, Th.J. de Boer and J.D.W. van Voorst, Tetrahedron 23, 4021 (1967).
14. J.G. Pacifici and H.L. Browning Jr., J. Amer. Chem. Soc. 92, 5231 (1970).
15. A.R. Forrester and S.P. Hepburn, J. Chem. Soc. C, 1971, 701
16. G. Boekestein and H.M. Buck, Rec. Trav. Chim. 92, 1095, (1973).
17. G. Boekestein, W.G. Voncken, E.H.J.M. Jansen and H.M. Buck, Rec. Trav. Chim. 93, 69 (1974).
18. Gerrit Boekestein, Eugène H.J.M. Jansen and Henk M. Buck, J. Chem. Soc., Chem. Comm. 1974, 118.

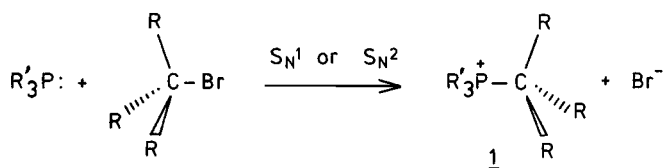
CHAPTER II

Charge transfer reactions of tris(dimethylamino)phosphine with activated bromides

II.1 Introduction

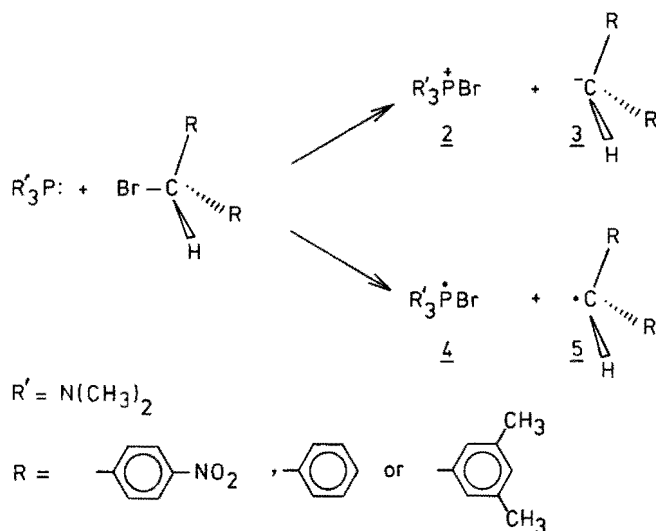
The preparation of phosphonium salts from phosphines and monohalides is the first step in the synthesis of "tailor-made" alkenes¹ (the Wittig reaction).

This simple addition can be described in terms of an S_N2 or S_N1 reaction, depending on the nature of the bromide, *i.e.* the magnitude of the substituent R:

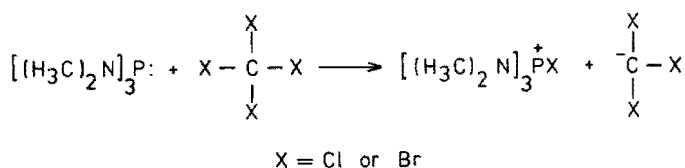


However, the strong nucleophilic tris(dimethylamino)-phosphine (TDAP) can be involved in an attack on the bromine atom instead of the central carbon atom. Two reactions may occur, *i.e.* homolytic or heterolytic cleavage of the C-Br bond, depending on the nature of both solvent and substituents of the original bromide (see reaction scheme next page).

The ion 3 is characterized by a strong colour and the radicals of type 4 and 5 can be measured directly by ESR or identified by the technique of spin-trapping, as described in Ch. I. In the case of the heterolytic cleavage a similar transfer of a bromonium ion is described by *Combret et al.*²



in the reaction of TDAP with carbontetrabromide or carbon-tetrachloride:



The intermediate products are postulated to account for the synthesis of alkenes from aldehydes.

II.2 Solvent effects and UV measurements

The reaction of TDAP with bis(p-nitrophenyl)methylbromide in diethylether results in the formation of the phosphonium salt. This was to be expected, but during the reaction a transient blue colour has been observed, too. Using the strong polar solvent benzonitrile the same colour was stable and very intense. The UV spectrum showed an absorption maximum at 710 nm. Absorption in the long-wave region indicates the presence of the bis(p-nitrophenyl)methyl anion. In com-

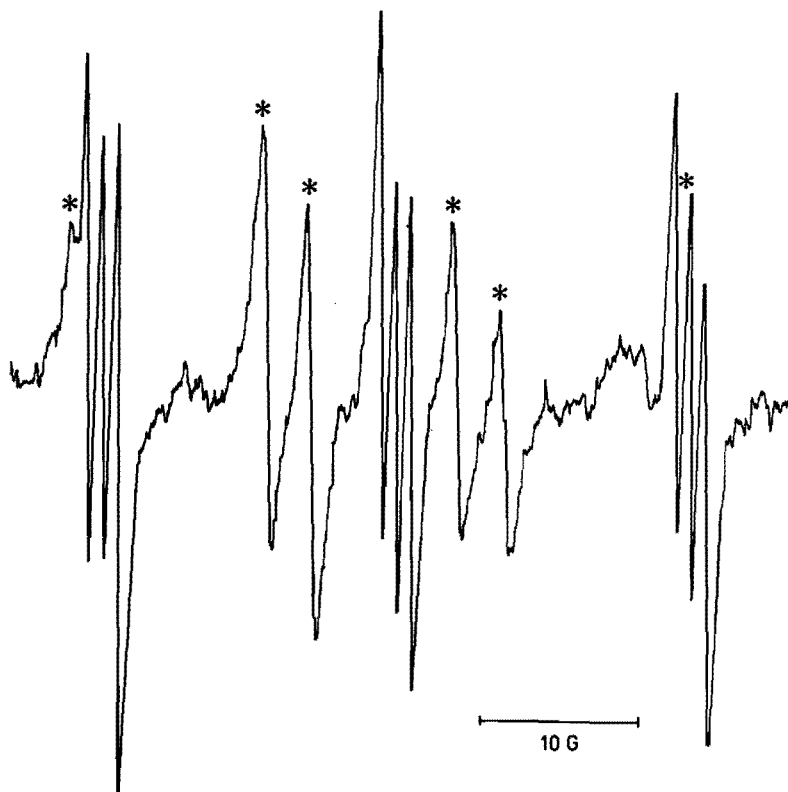
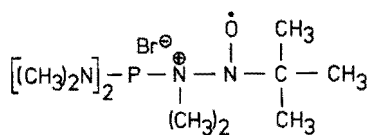


Fig. 2.1 - ESR spectrum of spin adducts 7 and 8, measured during the reaction of bis(p-nitrophenyl)methyl bromide with tris(dimethylamino)phosphine (TDAP) in the presence of the scavenger 2-methyl-2-nitrosopropane in DMF at -30°C . The lines marked with an asteriks are due to 7.



8

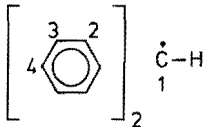
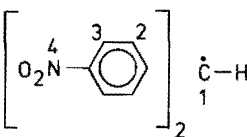
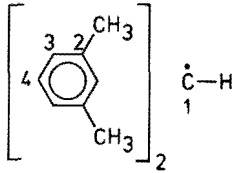
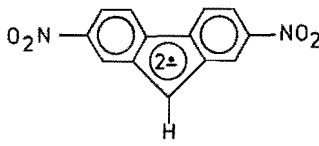
radical 7, appears. A shift of 2-methyl-2-nitrosopropane is involved here. The hyperfine splitting constants of the measured spin adducts (nitroxides) are given in Table II.1 and a comparison has been made with similar adducts, described by *Wajer et al.*³ and *Karlsson et al.*⁴.

Table II.1

Nitroxide	Solvent	ESR spectral data
$ \begin{array}{c} t\text{-Bu-N-C[PhNO}_2\text{]}_2 \\ \quad \\ \cdot\text{O} \quad \text{H} \quad \underline{6} \end{array} $	THF	$a_{\text{N}}=14.4 \text{ G}; a_{\text{H}}=2.1 \text{ G}$
$ \begin{array}{c} t\text{-Bu-N-C(CH}_3\text{)}_2 \\ \quad \\ \cdot\text{O} \quad \text{H} \end{array} $	<i>o</i> -xylene	$a_{\text{N}}=15.4 \text{ G}; a_{\text{H}}=1.4 \text{ G}^3$
$ \begin{array}{c} t\text{-Bu-N-P[N(CH}_3\text{)}_2\text{]}_3 \\ \\ \cdot\text{O} \quad \underline{7} \end{array} $	THF DMF (-30° C)	$a_{\text{N}}=10.3 \text{ G}; a_{\text{P}}=12.0 \text{ G}$ $a_{\text{N}}=11.9 \text{ G}; a_{\text{P}}=14.8 \text{ G}$
$ \begin{array}{c} \text{O} \\ \\ t\text{-Bu-N-P(OCH}_3\text{)}_2 \\ \\ \cdot\text{O} \\ -\text{Br}^- \end{array} $	H ₂ O	$a_{\text{N}}=10.3 \text{ G}; a_{\text{P}}=13.8 \text{ G}^4$
$ \begin{array}{c} t\text{-Bu-N-N}^{\oplus}\text{-P[N(CH}_3\text{)}_2\text{]}_2 \\ \quad \\ \cdot\text{O(CH}_3\text{)}_2 \quad \underline{8} \end{array} $	DMF (-60° C)	$a_{\text{N}}=18.4 \text{ G}; a_{\text{N}}=0.85 \text{ G}$

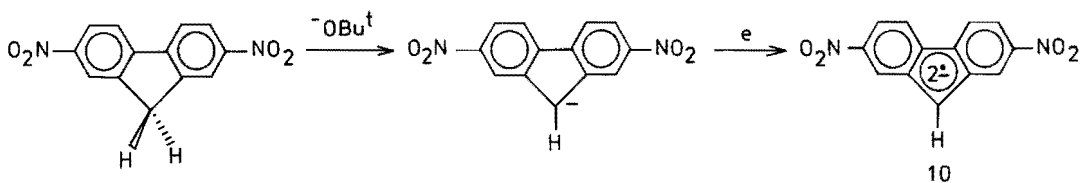
As already mentioned before, it was possible to measure a radical without the scavenger in DMF at -60°C . This radical could be characterized as the bis(p-nitrophenyl)methyl free radical, of which the spectral data are given in Table II.2. However, using diphenylmethyl bromide or bis(2,6-dimethylphenyl)methyl bromide, reaction with TDAP gave rise to the formation of more stable radicals.

Table II.2

	Position	$a_{\text{exp.}}(\text{G})$	$a_{\text{calc.}}(\text{G})$
	1	8.08	-17.42
	2	3.05	- 2.85
	3	1.25	1.28
	4	3.05	- 3.21
	1	8.8	-12.8
	2	2.6	- 2.9
	3	1.3	0.9
	4	<0.6	0.9
	1	16.30	-14.49
	2	2.21	3.15
	3	1.47	1.26
	4	3.26	- 3.22
	1	2.10	- 1.61
	2	0.47	3.71
	3	0.47	0.66
	4	2.59	- 2.28
	9	0.94	- 0.89

The transfer of bromine atoms from the bromide to the phosphine takes place at temperatures of 50° C and 100° C respectively, yielding high concentrations of the corresponding radicals. The spectra showed only slight differences, due to solvent effects, with the diphenylmethyl radical, which was dissolved in decalin⁵ and the bis(2,6-dimethylphenyl)methyl radical, dissolved in m-xylene⁶.

On the other hand, during the reaction of 2,7-dinitrofluorenylbromide with TDAP in DMF, a spectrum was recorded which can be ascribed to the 2,7-dinitrofluorenyl dianion radical (see section II.5). An identical spectrum was recorded, when 2,7-dinitrofluorene was allowed to react with potassium t-butoxide in DMF. The latter species has two properties: it is a strong base as well as a suitable reducing agent:



II.4 Spin density calculations

In order to verify the spectral data given in Table II.2, the spin-densities were calculated. The relatively simple Hückel procedure, followed by the approximate configuration-interaction treatment, developed by *McLachlan*⁷, appeared to be in better agreement with the experimental values, than the more sophisticated LCAO-MO-SCF methods.

In Table II.3 a comparison has been made for the diphenylmethyl radical. The results of the calculations, using the INDO method of *Pople, Santry and Segal*⁸, in which all valence electrons are included and the LCAO-MO-SCF method for open-shell molecules of *Bloor and Gilson*⁹, where the π -electron system is considered only, are given there .

Fig.2.2 - ESR spectrum of the bis(p-nitrophenyl)methyl free radical.

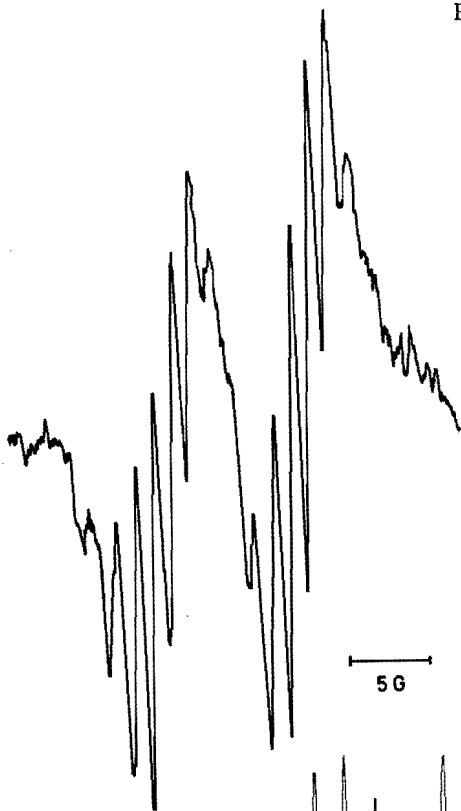


Fig.2.3 - ESR spectrum of the 2,7-dinitrofluorenyl dianion radical.

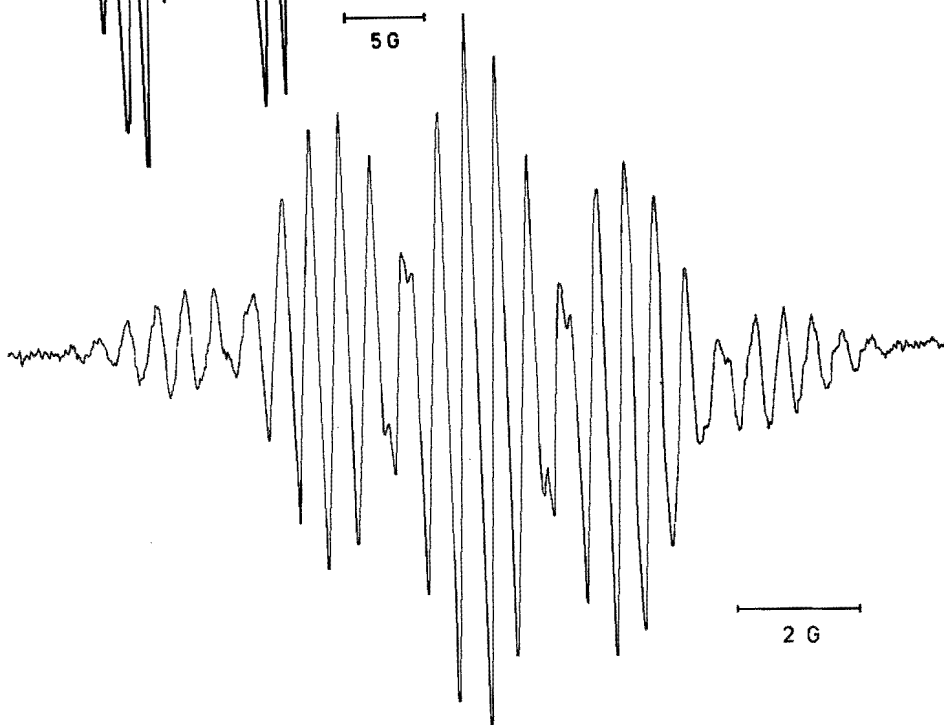
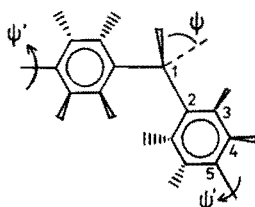


Table II.3



atom	$ a_{\text{exp}}^{\text{H}} $ ^{a)}	$a_{\text{calc}}^{\text{H}}$		
		McLachlan	INDO ^{b)}	open-shell ^{c)}
1	8.08	-17.42	-18.39	-18.02
3	3.05	- 2.85	- 3.52	- 2.35
4	1.25	1.28	2.18	0.62
5	3.05	- 3.21	- 2.73	- 1.49

a) Measured in DMF at 50^o C.

b) From s-orbital densities, $a^{\text{H}} = Q \cdot \rho_{\text{S}}^{\text{H}}$; $Q = +539.86$ G .

c) Parameters according to v.d. Hout-Lodder, $a^{\text{H}} = Q \cdot \rho^{\text{C}}$; $Q = 27$ G.

In the calculations, the molecule is assumed to be non-planar, *viz.* the angle ψ is 30^o which gives in the McLachlan calculation for the overlap integral $\beta_{1,2}$ a value of 0.9, while this molecular geometry is incorporated in the other calculations. However, all calculations showed a_{H} 's more than twice the value of measured one. According to *Dalton and Liebman*⁵ a different value for the proportionality-constant Q in the McConnell relation with respect to the central carbon atom must be applied, *viz.* -13.8 Gauss. This deviation is caused by a decreased overlap of the hydrogen orbital with a carbon sp^2 -orbital and Q is proportional to $\cos^2 \psi$ (see figure above Table II.3). With $Q = -13.8$ G, a_{H} of the atom attached to the central carbon atom is calculated to be -8.90 G with the carbon π -spin-density derived from the HMO-McLachlan calculation. From Table II.3 can be seen that the calculation mentioned above gave the best results with respect to the hyperfine splitting constants of the aromatic protons.

In the McLachlan theory, the atom-atom polarizabilities from a Hückel calculation are used to approximate a configuration interaction treatment. The formula for the polarizability in terms of the coefficients $c_{\mu i}^*$ of the atomic orbitals μ in the molecular orbitals i and the orbital energies ϵ_i , according to *Coulson and Longuet-Higgins*¹¹, is:

$$\pi_{\mu\nu} = -4 \sum_{i=1}^m \sum_{j=m+1}^n c_{\mu i} c_{\nu i} c_{\mu j} c_{\nu j} (\epsilon_i - \epsilon_j)$$

The summation over i refers to the occupied molecular orbitals, while the summation over j is over the orbitals of a bond not used in the wave function (unoccupied orbitals). The values of $\pi_{\mu\nu}$ are used to correct the Hückel spin densities ($c_{\mu 0}^2$) derived from the coefficients of the singly occupied MO. Finally, λ is an empirical constant given by $\lambda = 1.2 \beta^{11}$.

$$\rho_{\mu}^{\pi} = c_{\mu 0}^2 - \lambda \sum_{\nu} \pi_{\mu\nu} c_{\nu 0}^2$$

The Coulomb and Resonance integrals for other than carbon atoms are defined by the equations: $\alpha_x = \alpha + \delta_x \beta$ and $\beta_{xy} = \gamma_{xy} \beta$. The *Rieger and Fraenkel* parameters are given in Table IV¹². For the calculation of the hydrogen hyperfine splitting constants (a^H) from the carbon spin densities (ρ), the formula of *Colpa and Bolton*¹³ was used: $a_i^H = (-27.0 - 12.8q_i)\rho_i$. q_i and ρ_i are the excess electron density and spin density on atom i respectively. Methyl group splitting constants were obtained by applying the *McConnell* relation, where $Q = +25 \text{ G}^{11}$, while $a_N = 99\rho_N - 71.6\rho_O$ ¹³ was a good approximation of ^{14}N splitting constants. As can be seen in Table II.2 one large deviation of measured and calculated splitting constants is established, *i.e.* the nitrogen hyperfine splitting constant in the 2,7-dinitrofluorenyldianion radical. This is

*The indices of the atomic orbitals are indicated with μ and ν ; those of the molecular orbitals with i and j .

probably a consequence of the character of the *Rieger and Fraenkel* parameters, which are optimized for monoanion radicals.

Table III.4

x	y	δ_x	γ_{xy}
O	N	1.4	1.67
N	C	2.2	1.2
H ₃	C'	-0.5	2.5
C'	C	-0.1	0.9

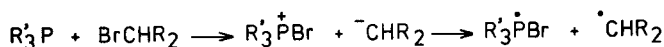
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{N} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$

$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{C}'-\text{H}_3 \end{array}$

II.5 Discussion

In accordance with the results, three different routes during the reaction of tris(dimethylamino)phosphine with substituted methyl bromides are proposed, depending on the nature of the solvent, as described in section II.1.

With respect to homolytic cleavage or heterolytic cleavage of the C-Br bond one could imagine an alternative mechanism, *i.e.* heterolytic cleavage, followed by electron transfer of the (substituted) diphenylmethyl anion towards the phosphonium ion:



This electron transfer should take place in less polar solvents (THF or DMF). However, electrolytic oxidation of the bis(*p*-nitrophenyl)methyl anion in DMF did not result in the formation of the corresponding radical. So, the electron transfer from the stable anion is impossible, even when ap-

plying more rigorous methods.

In diethyl ether the expected phosphonium salt formation takes place. In more polar solvents, homolytic or heterolytic cleavage of the C-Br bond occurs.

Using bis(p-nitrophenyl)methyl bromide, only heterolytic cleavage takes place in the most polar solvent benzonitrile; no paramagnetism is observed and a very intense colour appears, due to the formation of the anion. Obviously, the existence of ions is stabilized here by the solvent. In DMF or THF, however, heterolytic cleavage, in combination with homolytic cleavage, is to be considered. In these solvents the blue colour is observed, too, while the signal to noise ratio of the measured bis(p-nitrophenyl)methyl free radical is rather poor.

The reaction of TDAP with diphenylmethyl bromide and bis(2,6-dimethylphenyl)methyl bromide, where the electron-withdrawing nitro group has been replaced, only homolytic cleavage is observed, resulting in ESR signals of increased intensity.

During the reaction of TDAP with 2,7-dinitrofluorenyl bromide the corresponding dianion radical was measured.

A first indication in the spectrum is the absence of a large hyperfine splitting constant, due to the proton attached to the central carbon atom.

In the fluorenyl free radical the coupling constant of this atom is recorded as 7.0 G⁵ and our spin density calculations on the dinitro-substituted analogon gave a value of 13.6 G. However, the fluorenyl dianion radical is relatively stable^{1*}. Spin density calculations, based on the dianion radical, were in proper agreement with the data derived from the experimental spectrum. An explanation of the formation of the dianion radical can be found in the electron donating properties of phosphines towards electron accepting molecules (see Ch. III and IV).

The radical might be formed either by heterolytic cleavage or homolytic cleavage of the C-Br bond, followed by a one or two electron transfer, respectively:

References

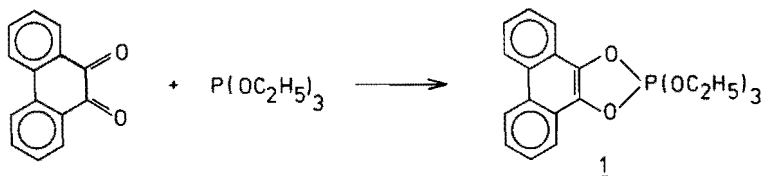
1. A.W. Johnson, Organic Chemistry - Volume 7, Academic Press (1966).
2. J.C. Combret, J. Villières and G. Lavielle, Tetrahedron Lett. 15, 1035 (1971).
3. Th.A.J.W. Wayer, A. Mackor and Th.J. de Boer, Tetrahedron 23, 4021 (1967).
4. H. Karlsson and C. Langercrantz, Acta Chem. Scand. 24, 3411 (1970).
5. D.A. Dalton and S.A. Liebman, J. Amer. Chem. Soc. 91, 1194 (1969).
6. J. de Jong, K.H. Fleurke and R. van Hardeveld, Rec. Trav. Chem. 85, 284 (1966).
- 7a. A.D. Machlan, Mol. Phys. 1, 233 (1958).
- b. A.D. Machlan, Mol. Phys. 3, 233 (1960).
- 8a. J.A. Pople, D.P. Santry and G.A. Segal, J. Chem. Phys. 43, S 129 (1965).
- b. J.A. Pople and D.L. Beveridge, Approximate Molecular Theory, McGraw-Hill (1970).
9. J.E. Bloor and B.R. Gilson, computer program from Quantum Chemistry Program Exchange, Indiana University, U.S.A.
10. A.E. van der Hout-Lodder, Thesis Eindhoven (1972).
11. C.A. Coulson and H.C. Longuet-Higgins, Proc. Roy. Soc. A 191, 39 (1947); A 192, 16 (1947).
12. P.H. Rieger and G.K. Fraenkel, J. Chem. Phys. 39, 609 (1963).
13. J.P. Colpa and J.R. Bolton, Mol. Phys. 6, 273 (1963).
14. N.L. Bauld and J.H. Zoeller Jr., Tetrahedron Lett. 10, 885 (1967).

CHAPTER III

Charge transfer reactions of trivalent phosphorus compounds with activated carbonyl compounds

III.1 Introduction

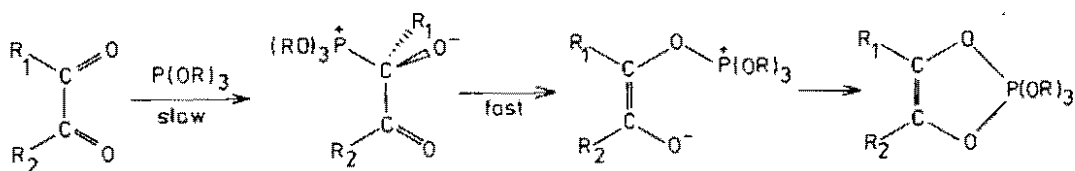
It has been shown that trivalent phosphorus compounds are able to react with carbonyl functions¹. This property is used for the synthesis of a wide variety of five-membered cyclic oxyphosphoranes. A typical example is the formation of oxyphosphorane 1 from triethylphosphite and 9,10-phenanthrenequinone.



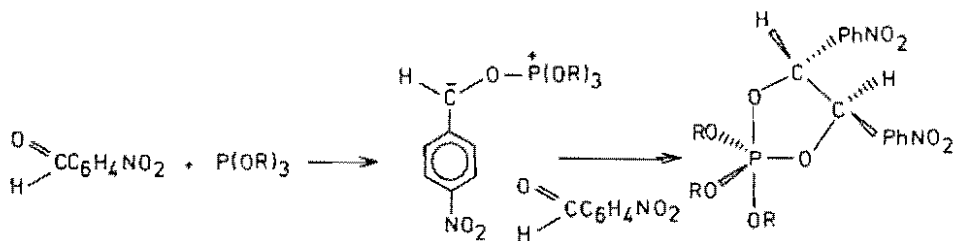
This kind of reactions is carried out under very mild conditions and high yields of oxyphosphoranes are usually obtained. The aim of the investigation, described in this chapter, is to offer a suitable reaction mechanism which is in good correspondence with our observations. Although these reactions are simple 1:1 additions, there is much confusion in the literature about the real mechanism and several deviations of the indicated reaction sequence will occur (*e.g.* 1:2 additions and rearrangements).

*Ogata et al.*² proposed an ionic mechanism for this type of reaction. Based on their kinetic studies of the reactions of alifatic and aromatic α -diketones with trimethylphosphite, they presumed that the primary and rate-determining step is

a nucleophilic attack of the phosphorus atom on a positively charged atom of the carbonyl group. The following steps consist of a fast rearrangement of the dipolar ion, leading to ring closure:



The reaction of trialkylphosphites with suitably activated monocarbonyl compounds leads to the formation of 2:1 adducts, *viz.* 1,3,2-dioxaphospholanes. Ramirez³ stated the formation of a 1:1 adduct as a primary step. This adduct is the result of the attack by the phosphorus atom on the carbonyl oxygen atom:



On the other hand similar reactions, involving radicals, are reported by Lucken *et al.*⁴ (triphenylphosphine with chloranil) and Ogata *et al.*⁵ (trimethylphosphite with acenaphthequinone). The experiments described in section III.2 strongly indicate, that in reactions between trivalent phosphorus compounds and activated ketones (α -diketones, o -quinones and α, β -unsaturated ketones) electron transfer takes place. The different radicals are recognized and the reaction model for the formation of oxyphosphoranes and related compounds is based on these observations.

III.2 Results

A. Reaction of TDAP with 9,10-phenanthrenequinones

In a first experiment solutions of 10^{-2} Mol/l $P\{N(CH_3)_2\}_3$ and 10^{-2} Mol/l 9,10-phenanthrenequinone in CH_2Cl_2 were mixed in a flow system. Two different radicals were measured (Figure 3.1).

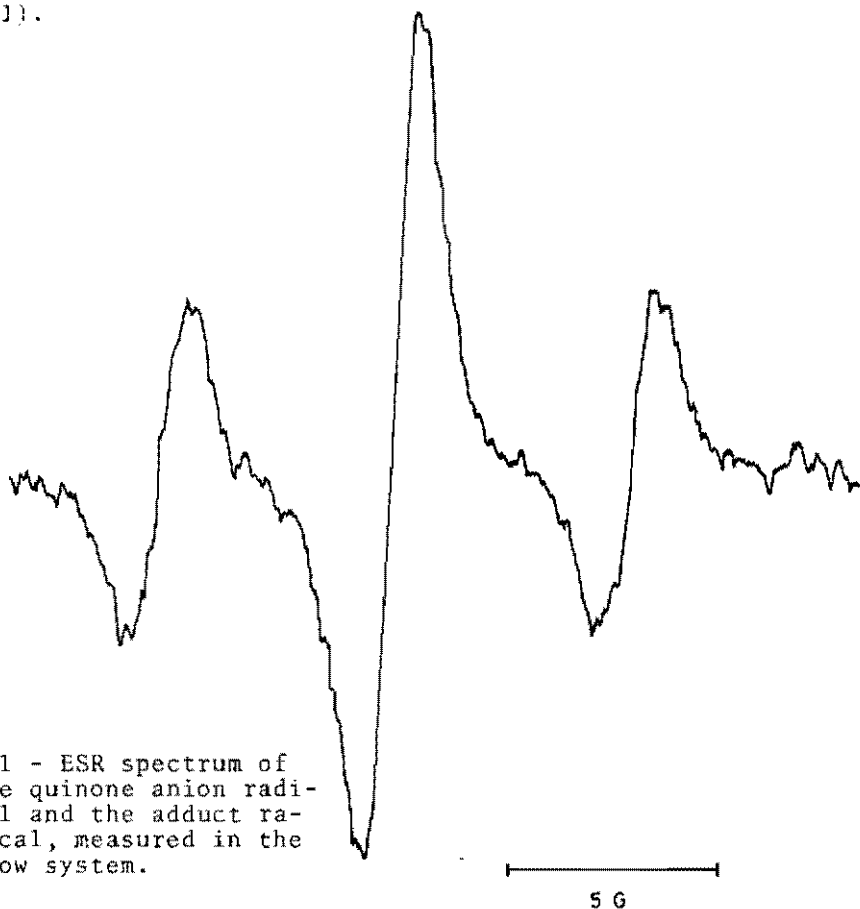
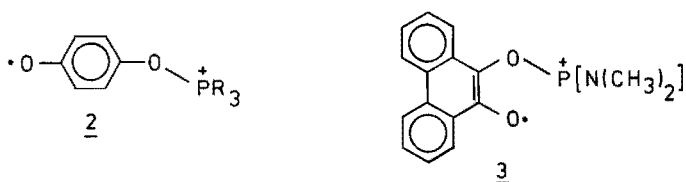


Fig. 3.1 - ESR spectrum of the quinone anion radical and the adduct radical, measured in the flow system.

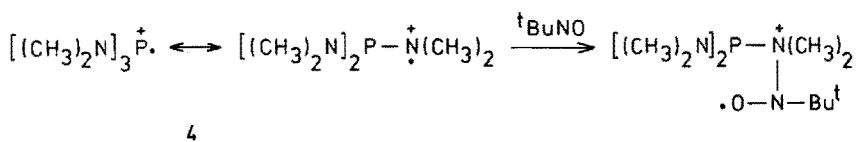
The central line indicates the presence of the 9,10-phenanthrene anion radical, while the other two lines (hyperfine splitting constant 11.2 G) may be a doublet from a radical containing phosphorus. This value is of the same magnitude

as found in the radicals described in Ch. IV (2). So in this case the formation of radical 3 is proposed:



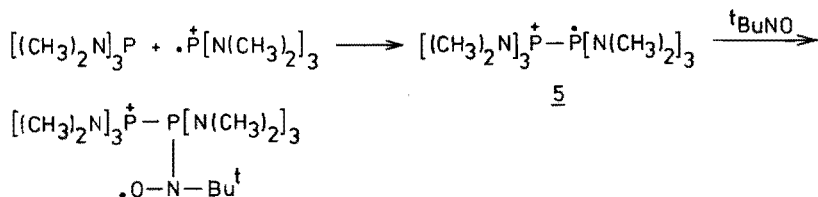
In order to identify the intermediate radicals appearing in this reaction, the technique of spin trapping was applied (see Ch. I and II). To a solution of 2-methyl-2-nitrosopropane and the quinone in benzene, tris(dimethylamino)phosphine was added.

The ESR spectrum showed a triplet of triplets, due to two non-equivalent nitrogen nuclei of trapped phosphinium radicals (4):



The phosphinium radicals are formed by an electron transfer from the phosphine to the quinone. However, the 9,10-phenanthrenequinone anion radical was not observed under these conditions.

When an excess of phosphine was used, a different spectrum was recorded, showing a triplet and two doublets. The doublets could be due to two non-equivalent phosphorus nuclei. The measured radical is probably a trapped dimeric phosphorus radical (5), formed in the reaction:



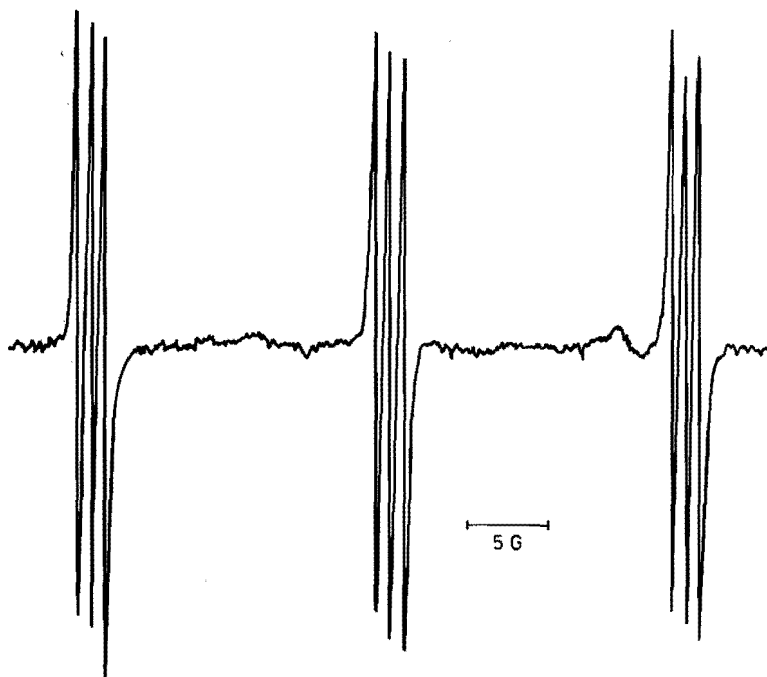


Fig. 3.2 - ESR spectra of the adduct radicals of 2-methyl-2-nitrosopropane with the monomeric phosphinium radical 4 (above) and the dimeric radical 5.

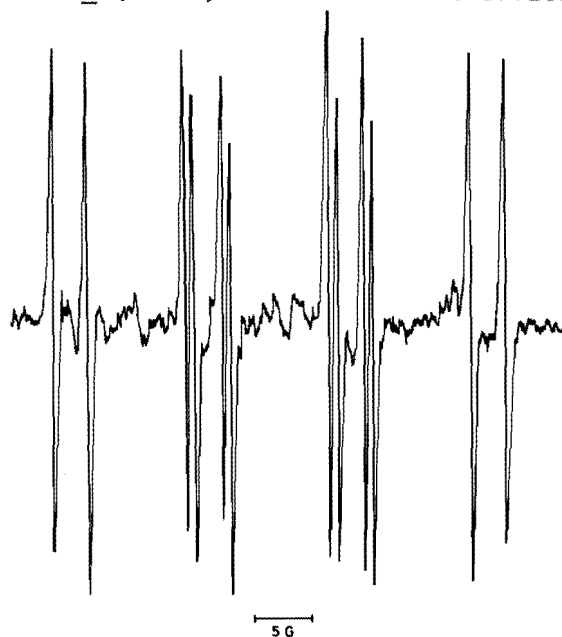
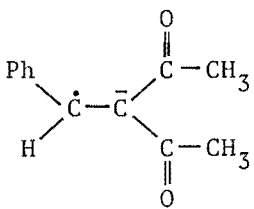
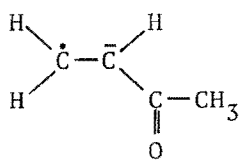


Table III.1

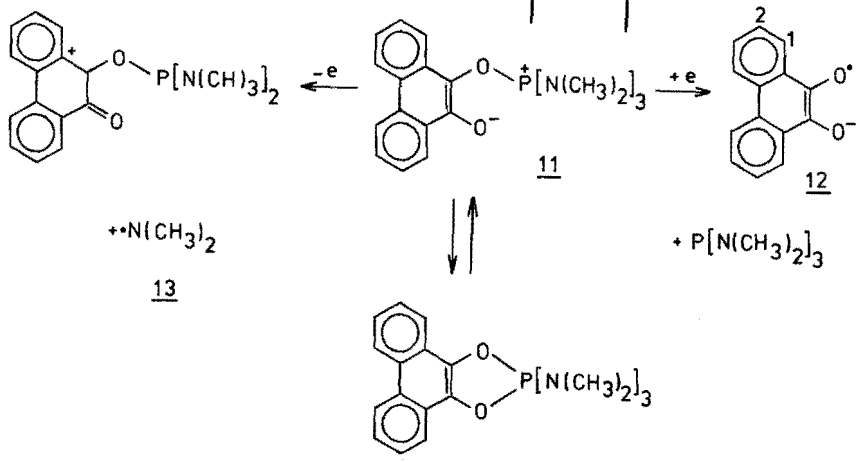
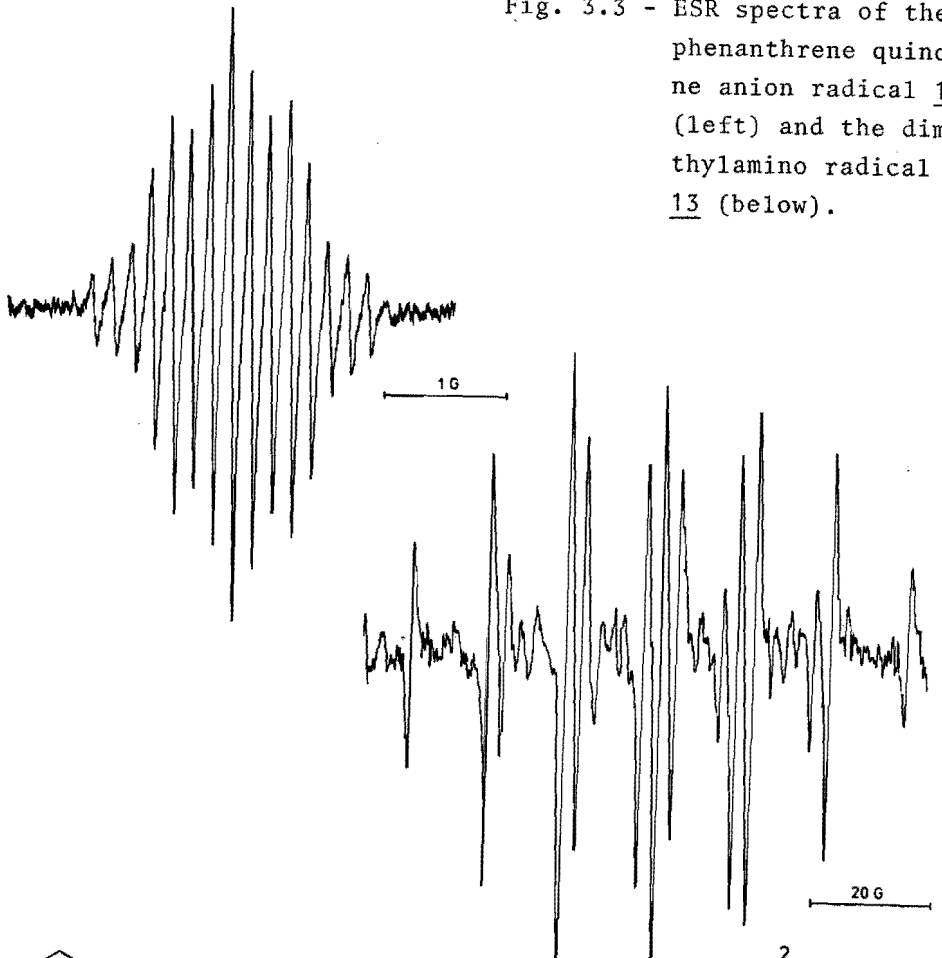
Trapped Radical	Solvent	Hyperfine splitting constants (G)		
		a_N	a_P	a_H
$[(CH_3)_2N]_2P-\dot{N}(CH_3)_2$ (4)	Benzene	18.5; 0.9		
$[(CH_3)_2N]_3P-\dot{P}[N(CH_3)_2]_3$ (5)	Benzene	12.2	11.5; 3.1	
$\dot{P}(OC_2H_5)_3$ (6)	Benzene	13.3	11.2	
$\cdot C_2H_5$ (7)	Benzene	15.4		10.7
$\cdot CH_3$ (8)	Benzene	15.7		11.8
 (9)	CH_2Cl_2	15.0		5.7
 (10)	CH_2Cl_2	15.8		13.1

The same spin adducts were measured using 2,7-dinitrophenanthrenequinone.

B. Reaction of trialkyl phosphites with 9,10-phenanthrenequinones.

Adding an excess of triethyl phosphite to a mixture of 2,7-dinitrophenanthrenequinone and 2-methyl-2-nitrosopropane

Fig. 3.3 - ESR spectra of the phenanthrene quinone anion radical 12 (left) and the dimethylamino radical 13 (below).



D. Reaction of TDAP with acenaphtenequinone and 3,4-dinitro-acenaphtenequinone

The reaction of acenaphtenequinone with TDAP in benzene/THF gave rise to the formation of a radical with a rather complicated ESR spectrum (Figure 3.6), showing a main septet of triplets with additional hyperfine structure. The large number of lines indicates the presence of a 2:1 adduct radical. On the other hand, similar reaction with 3,4-dinitro-acenaphtenequinone gave rise to the formation of the corresponding quinone anion radical which is stabilized by the nitro groups ($a_H=1.75$ G, $a_N=0.4$ G) like the dinitrophenanthrene anion radical.

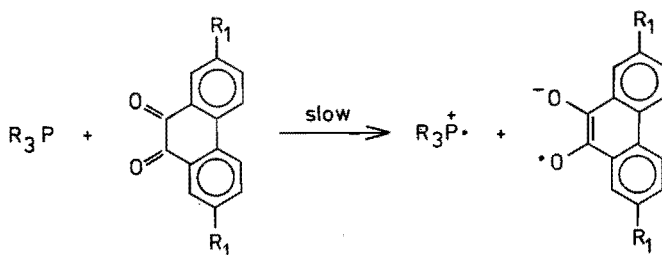
E. Reduction and oxidation of oxyphosphorane 11

Attempts to get a better-resolved spectrum of radical species 3 by means of electrochemical oxidation of the parent compound 11 in DMF or CH_2Cl_2 failed. However, chemical oxidation by PbO_2 or benzoylperoxide leads to the formation of dimethylamino radicals (Figure 3.3; $a_N=14.90$ G, $a_{CH_3}=10.23$ G). On the other hand, electrolytic reduction in CH_2Cl_2 leads to the formation of the phenanthrenequinone anion radical ($a_H^1=0.97$ G, $a_H^2=0.32$ G). Apparently, the adduct dissociates by this treatment. So, radical 3 can only be measured as an intermediate during the reaction of TDAP with phenanthrenequinone.

III.3 Discussion

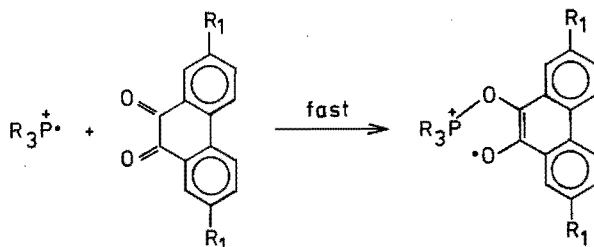
From the ESR measurements it is clear that radicals are intermediates in the reaction of phosphites or phosphines with *o*-quinones or α,β -unsaturated ketones, yielding oxyphosphoranes.

The first step is an electron transfer from the phosphorus compound to the quinone:



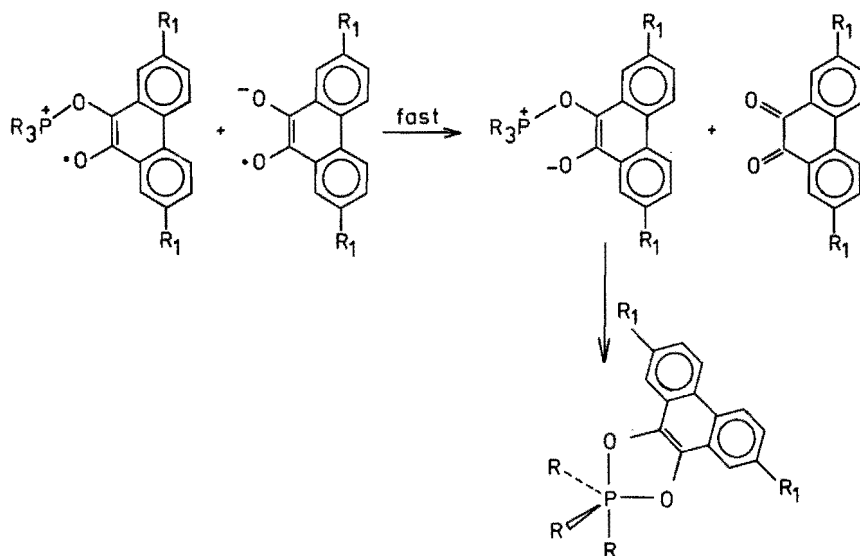
Both radicals could be detected, *viz.* the phosphonium radical as a spin adduct with the scavenger 2-methyl-2-nitrosopropane and the quinone radical if it was stabilized by nitro groups ($R_1 = \text{NO}_2$). When $R_1 = \text{H}$, the quinone anion radical was detected in the flow experiment.

The phosphonium radical must be highly reactive (not detected in the flow experiment), so it reacts rapidly with a carbonyl function, yielding an adduct radical:

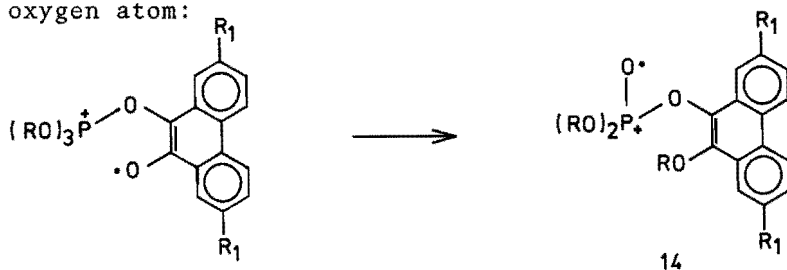


This adduct produced the doublet in the flow experiment $R = \text{N}(\text{CH}_3)_2$.

This doublet cannot be attributed to the phosphonium radical, for no nitrogen splittings were observed. The adduct radical is readily reduced by the anion radical, produced in the first step, to the open dipolar oxyphosphorane, which normally gives the closed five co-ordinated oxyphosphorane (if $R = \text{N}(\text{CH}_3)_2$ the dipolar structure is favoured⁶):



In some cases, if $R=CH_3$ or CH_2CH_3 , the adduct radical isomerizes by alkyl radical transfer from an alkoxy group to the oxygen atom:



Although this must be a very fast rearrangement, these radicals can be trapped by the scavenger, because of the high concentration of the latter species. The phosphate radical might be reduced by a quinone anion radical, according to the third step in the reaction mechanism. Further evidence for the formation of the phosphate ester 14 was found in the PMR spectrum of the reaction product of trimethylphosphite and 9,10-phenanthrenequinone (a singlet from the methoxy group at $\delta=3.22$ ppm, two doublets at $\delta=3.62$ and 3.55 ppm, figure 3.6). The intensity ratio of the doublets is approximately 1:4 (the low-field signal is the most intensive) which

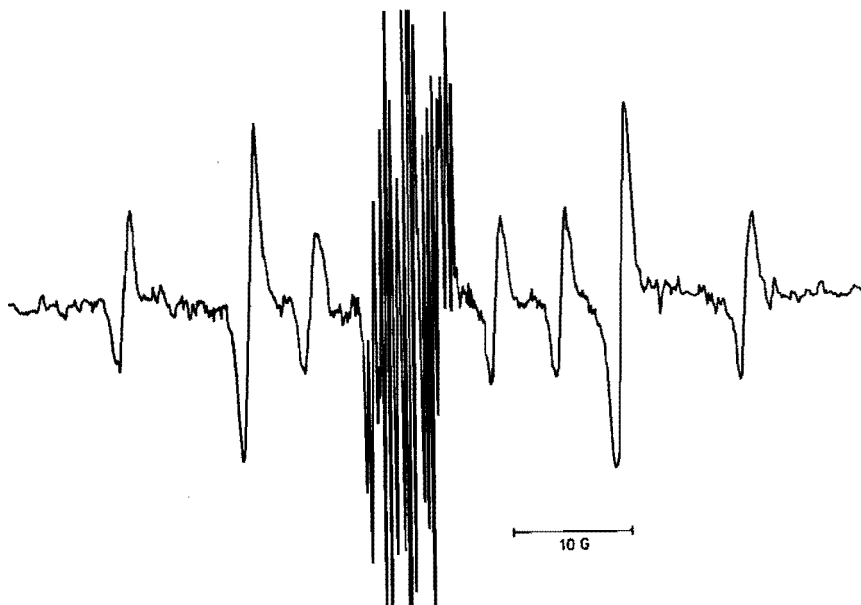


Fig. 3.4 - ESR spectrum of the trapped ethyl radical (broad lines) and the 2,7-dinitrophenanthrenequinone anion radical.

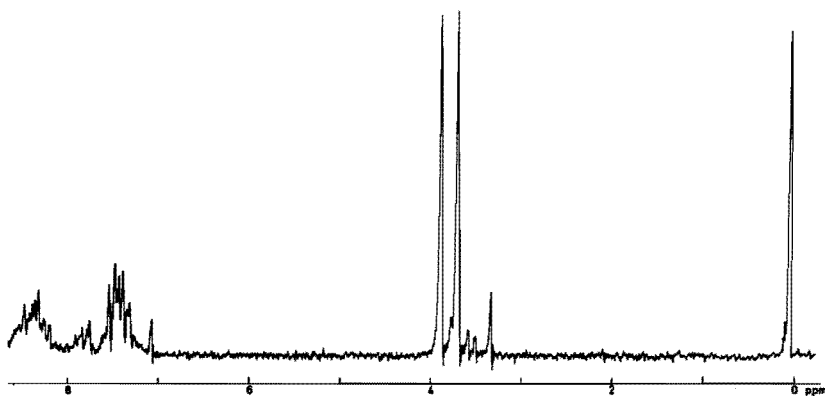
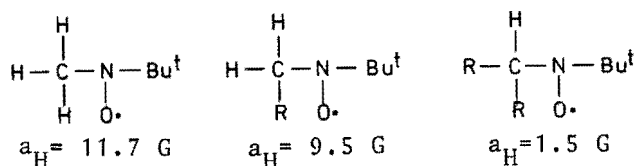


Fig. 3.5 - PMR spectrum of the adduct of phenanthrenequinone with $(\text{CH}_3\text{O})_3\text{P}$ and the related phosphate ester 14.

corresponds with the distribution of the two isomers in the mixture. A similar rearrangement is described in Ch. IV in the reaction of trivalent phosphorus compounds with p-quinones.

In the reaction of α,β -unsaturated ketones with alkyl phosphites reduced α,β -diketone radicals were trapped, which is another argument for the strong electron donating properties of trivalent phosphorus compounds.

It may be seen from Table III that the value of the hydrogen splitting constants of the spin adducts decreases by the number of hydrogen atoms attached to the carbon atom at which the short-lived radicals are trapped. This is in good agreement with the observations of *Wajer*⁷ who described the following series of nitroxides:

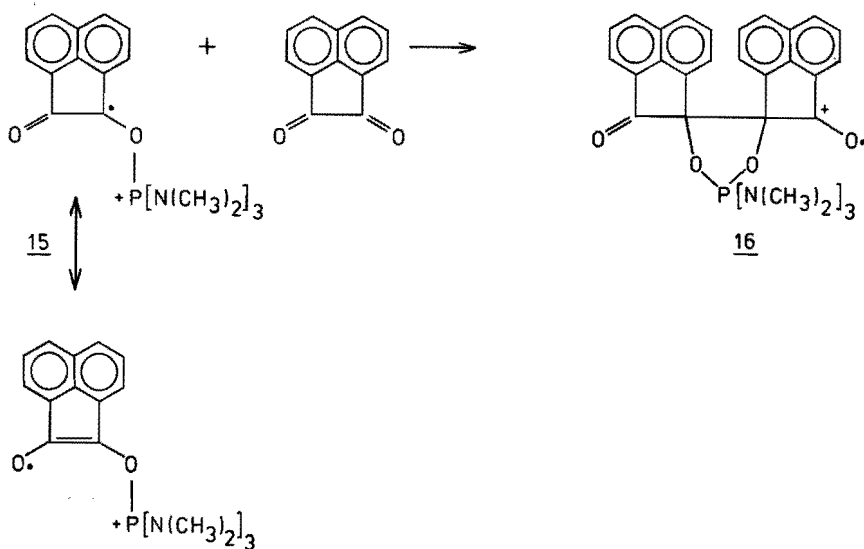


An explanation of this effect can be found in the hyperconjugation mechanism which, in general, can be applied to β -coupling⁸.

In addition to the experiments described in section III.2, *Ogata et al.*⁵ reported the appearance of quinone anion radicals in the reaction of acenaphtenequinone with trimethylphosphite. However, they still considered a radical mechanism less important than the ionic mechanism they previously proposed. Phosphinium cation radicals, produced in the first step, were observed by the rate of disappearance of diphenylpicrylhydrazine (DPPH), involving an electron transfer from DPPH to the phosphinium radicals. The reaction rate was measured by means of UV-VIS spectrophotometry. In the reaction scheme proposed here there could be a competition between the addition of phosphine to the neutral quinone (second step) and a reaction with DPPH, so a comparison of the con-

sumption rate of the quinone and the rate of disappearance of DPPH ($k=2.10^{-2}\text{sec}^{-1}$ vs $k=1.6.10^{-6}\text{sec}^{-1}$) does not rule out a radical mechanism as suggested by these authors. Furthermore, the concentration of DPPH has to be very low (in order to carry out UV measurements) in comparison with the quinone concentration, which accounts for the difference observed in the reaction rate of a factor 10^4 .

During the reaction of acenaphtenequinone with TDAP it is possible to detect a radical related to the one produced in the second step of the reaction. As mentioned in section III.2 this must be a 2:1 adduct radical and attempts to obtain similar radicals by other means were fruitless. The adduct radical 15 is able to react with a neutral molecule of acenaphtenequinone, yielding radical species 16 (Fig. 3.6):



In the spectrum a septet of triplets with additional hyperfine structure is recognized easily, while a closer look at the spectrum (modulation amplitude = 0.05 G) shows that each line consists of a triplet of quintets. So, 14 nuclei with $I=\frac{1}{2}$ are available theoretically. However, only 13 nuclei of this kind can be seen in radical 16, namely twelve aroma-

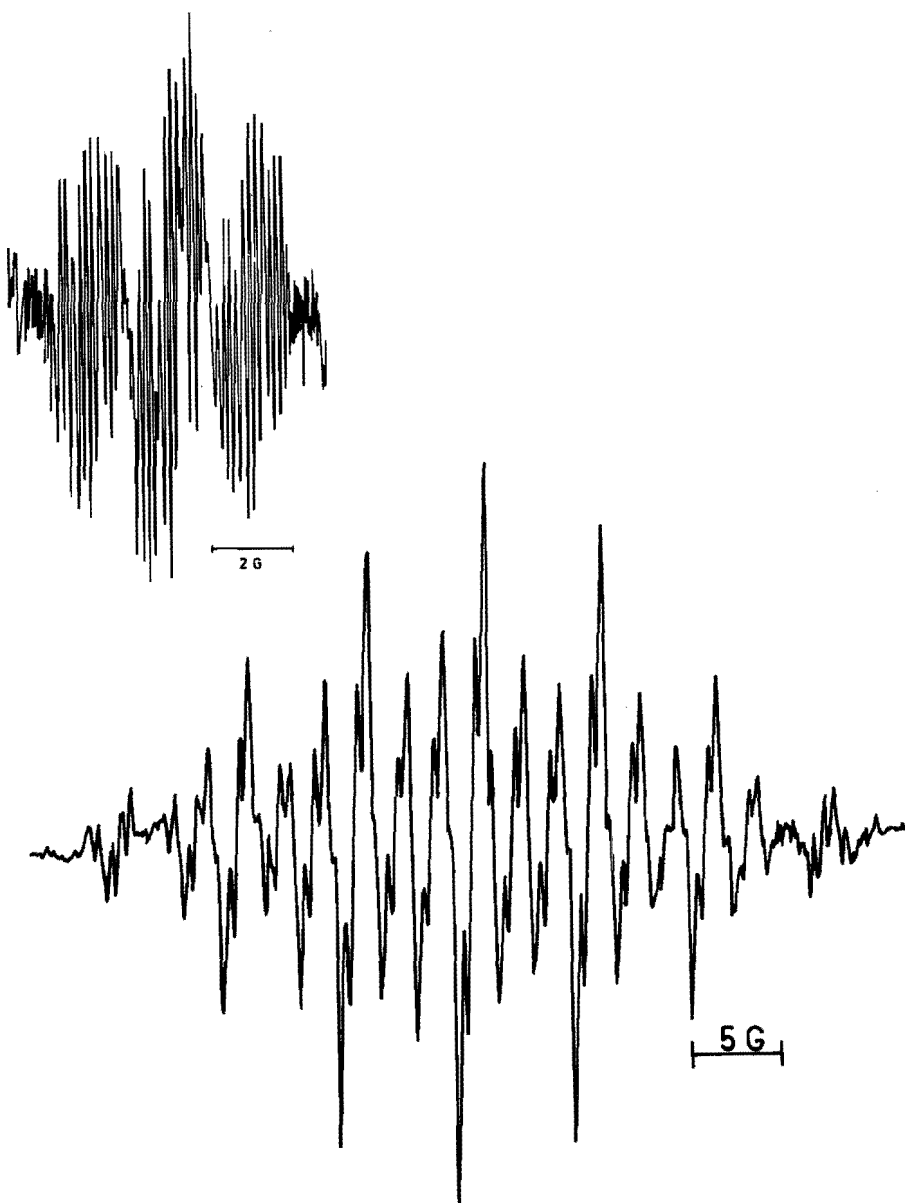


Fig. 3.6 - ESR spectra from the reaction of acenaphtenequinone with TDAP yielding the 2:1 adduct radical 16. The upper part of the figure is an expanded triplet signal, of which seven groups are present in the spectrum below (see text).

tic hydrogen and one phosphorus atom. This can be explained by assuming the phosphorus splitting constant approximately twice as large as the one from a pair of equivalent hydrogen atoms, resulting in an intensity ratio of 1:2:2:2:1. The nitrogen atoms are not taken into account, while the unpaired electron is located at a considerable distance from these nuclei. The reaction of TDAP with 3,4-dinitroacenaphtenequinone only gave rise to the formation of the corresponding quinone anion radical (see Section III.2).

So, 1:1 and 2:1 additions of quinones and ketones with trivalent phosphorus compounds do obey this three-step reaction scheme.

In order to exclude the possibility of another (ionic) mechanism p-nitrobenzaldehyde and trimethylphosphite were mixed in the presence of an excess of 2-methyl-2-nitrosopropane in CH_2Cl_2 for 40 hours. No 2:1 adduct was formed, because the intermediate radicals were trapped by the scavenger.

References

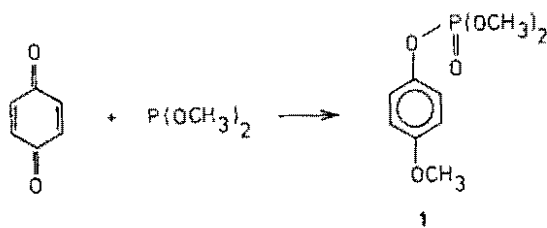
1. F. Ramirez, *Synthesis* 1974, 90.
- 2a. Y. Ogata and M. Yamashita, *Tetrahedron* 27, 2725 (1971).
b. Y. Ogata and M. Yamashita, *ibid* 27, 3395 (1971).
c. Y. Ogata and M. Yamashita, *J. Org. Chem.* 36, 2584 (1971).
3. F. Ramirez, S.B. Bhatia and C.P. Smith, *Tetrahedron* 23, 2067 (1967).
4. E.A.C. Lucken, F. Ramirez, V.P. Catto, D. Rhum and S. Dershowitz, *Tetrahedron* 22, 637 (1966).
5. Y. Ogata and M. Yamashita, *J. Org. Chem.* 38, 3423 (1973).
6. F. Ramirez, A.V. Patwardhan and C.P. Smith, *J. Amer. Chem. Soc.* 87, 4973 (1965).
7. Th.A.J.W. Wajer, Thesis Amsterdam (1969).
8. A. Carrington and A.D. McLachlan, *Introduction to Magnetic Resonance*, Harper and Row (1969).

CHAPTER IV

Charge transfer reactions of trivalent phosphorus compounds with para-quinones

IV.1 Introduction

This chapter deals with the reactions of trivalent phosphorus compounds with various p-quinones. Efforts are undertaken to explain for the formation of the different products, while in the literature the attention was focussed on one aspect of these reactions. For example, *Ramirez et al.*¹ found that in the reaction of p-benzoquinone with trimethylphosphite the methyl ether of p-quinoldimethylphosphate was formed.



On the contrary, *Lucken et al.*² described the formation of radical 2, where the phosphorus atom is attached to the phenyl ring.

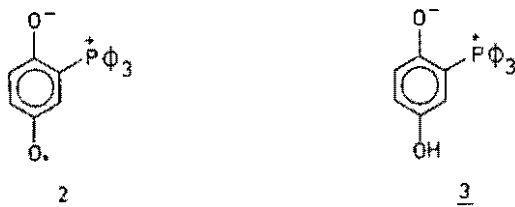
In fact, both reactions can be explained in terms of a one electron transfer from the phosphorus compound to the quinone, followed by the attack of the phosphorus cation radical to a new quinone molecule, analogous with reactions described in Ch. III. The phosphorus cation radical in this case has the possibility of attacking on two sites of the p-quinone molecule, which results in the formation of the two

different products. Both reactions can pass at the same time, for instance in the reaction of trimethylphosphite with p-benzoquinone. However, in some cases one reaction does not take place somehow and one product is formed exclusively.

IV.2 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 a 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 above-mentioned colour was visible. The yellow precipitate has according to experiments of Ramirez³ structure 3.



This experiment leads to the conclusion that an orange-red radical should be the reaction intermediate. The spectral data of this radical (Table IV.1) can only be interpreted in terms of structure 2. 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 4 was mainly formed ($\delta_{\text{OCH}_3} = 3.77$ ppm; $\delta_{\text{P}(\text{OCH}_3)_2} = 3.83$ ppm; $\delta_{\text{Phenyl}} = 6.87$ and 7.17 ppm; $^3J_{\text{P}} = 11.7$ Hz; $J_{\text{Phenyl}} = 9.8$ Hz).

These observations indicate that two reactions occurred simultaneously.

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). This observation is like the one described in the preceding chapter, indicating a similar alkyl radical transfer (see also section IV.3).

During the reaction of p-benzoquinone with tris(dimethyl-amino)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 4.1). This is an indication that the radicals formed during the reaction are unstable. For this reason no PMR-spectrum could be obtained either. The ESR spectrum was like the one obtained by the reaction with trimethylphosphite interpreted in terms of radical type 2.

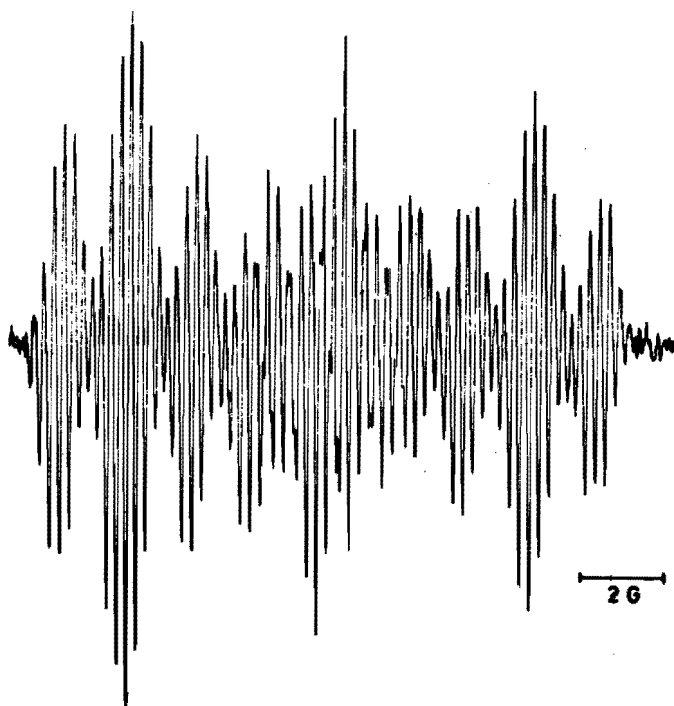


Fig. 4.1 - ESR spectrum of the radical adduct of p-benzoquinone and TDAP in benzene (type 2)

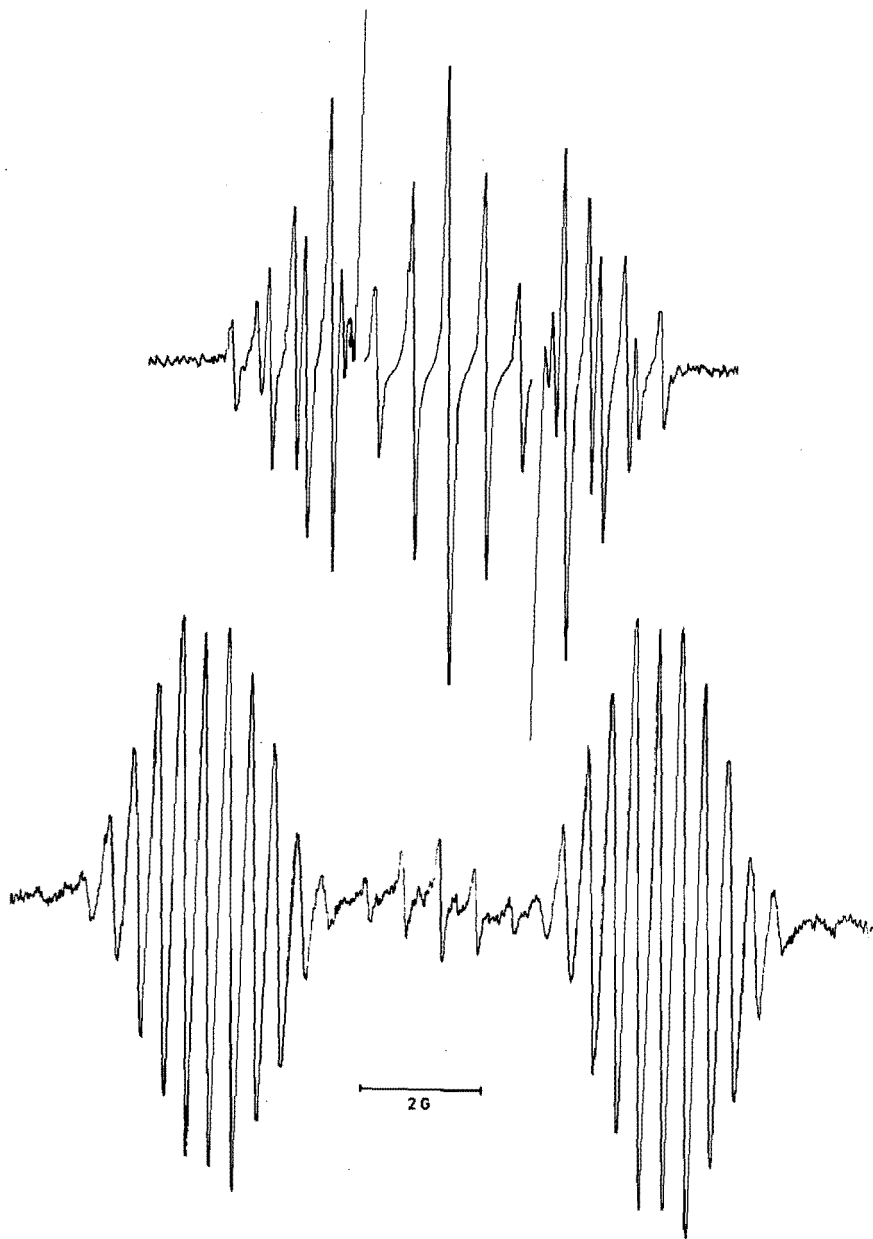
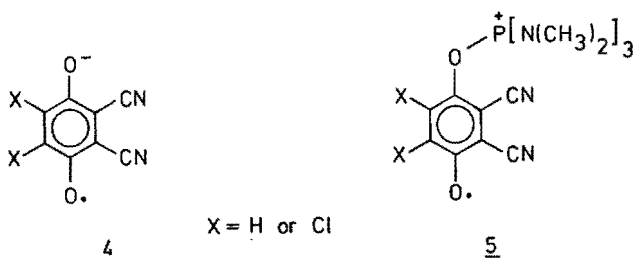


Fig. 4.2 - ESR spectra of the DDQ anion radical (above) and the adduct radical of DDQ and TDAP (below) in benzene.

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 ($a_{\text{N}}=0.59$ G, $a_{\text{C}}=2.42$ 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 has to be 5.



As can be seen in Figure 4.2 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 2 (0.59 and 0.24 G respectively).

C. The reaction of 2,3-dicyano-p-benzoquinone with TDAP

In this quinone two sites can be attacked by a phosphonium 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 must have been formed. In some experiments, however, where an excess of the quinone was used, an unstable radical of type 2 (two doublets of quintets) was measured ($a_{\text{H}} \approx a_{\text{P}} = 3$ G).

The stable radical has an additional fine structure of five nitrogen and two hydrogen atoms of which the coupling constants are solvent-dependent (see Table IV.2).

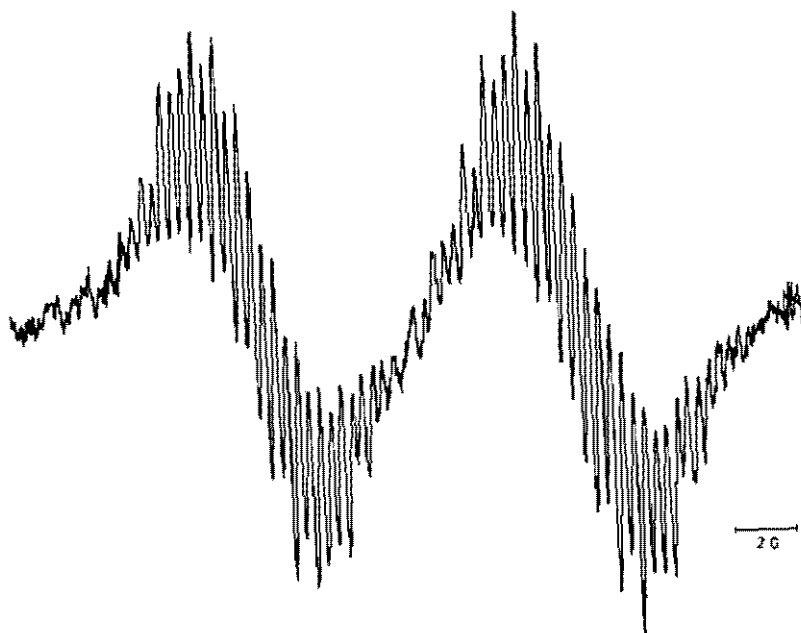


Fig. 4.3 - ESR spectra of 2,3-dicyano-p-benzoquinone anion radical in DMF (left) and the adduct radical of the quinone with TDAP in benzene.

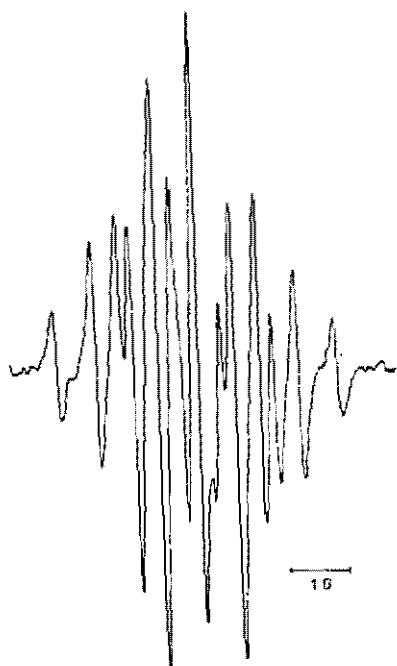
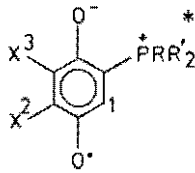
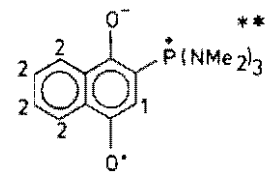


Table IV.1

									
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	**

During this reaction no p-quinone anion radical was measured. The spectrum of this radical was obtained by electrolysis in dimethoxyethane and the spectral data are given in Table IV.2. Although supplemental ^{13}C -lines were visible, the intensity of the signal was too weak to obtain the correct hfs constants.

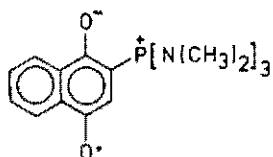
Finally, reaction of both cyano-substituted quinones with trialkylphosphites did not give a paramagnetic solution, which is to be explained in section IV.3.

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 remarkable features: a small phosphorus hfs constant (2.28 G and 2.42 G respectively) and a large line width. The radicals must 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 (see section IV.4).

E. Reaction of 1,4-naphtoquinone with TDAP

An ESR signal of high intensity was measured in this case due to the formation of a radical of type 2 possessing the following structure:



The hfs constants of this radical are given in Table IV.1 and are comparable to the data given by Lucken² in which other phosphines are used.

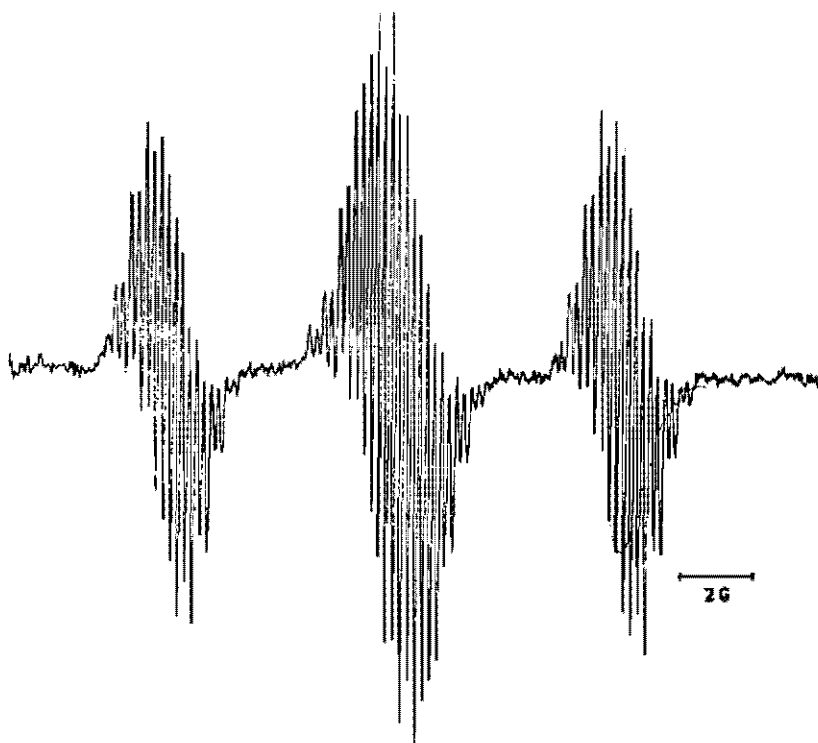
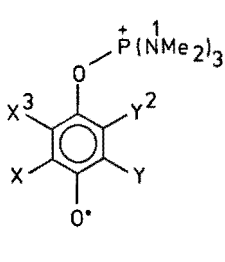
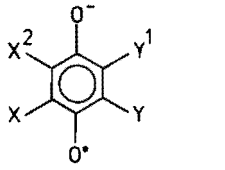


Fig. 4.4 - ESR spectrum of the adduct radical of TDAP with 1,4-naphtoquinone in benzene.

Table IV.2

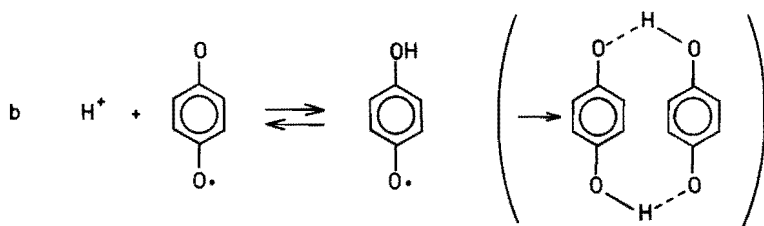
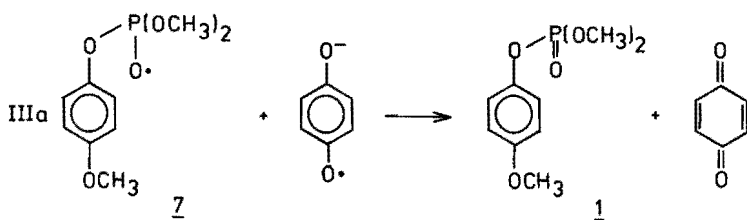
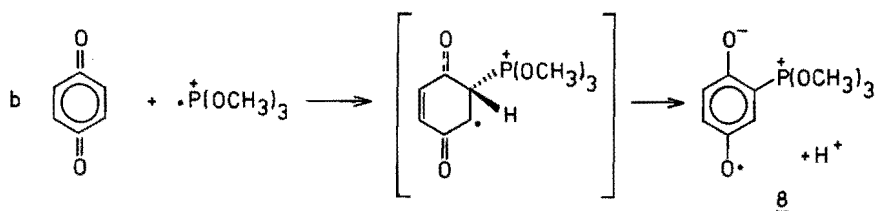
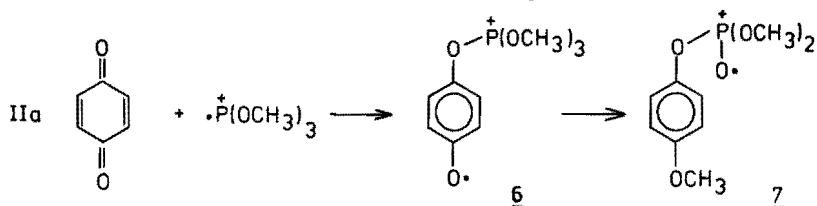
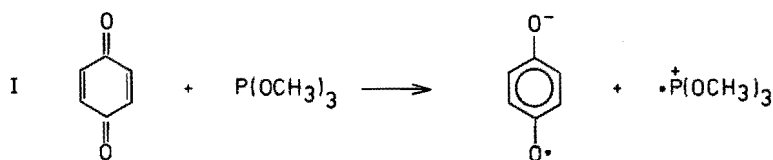
	<u>X</u>	<u>Y</u>	<u>Solvent</u>	<u>a_p</u>	<u>a₁</u>	<u>a₂</u>	<u>a₃</u>
	Cl	Cl	C ₆ H ₆	2.28	<0.8		
	Cl	CN	C ₆ H ₆	7.53	0.49	0.49	
	H	CN	C ₆ H ₆	10.61	0.36	1.08	1.80
	H	CN	C ₆ H ₆ / CH ₂ Cl ₂	10.75	0.42	1.19	1.95
	H	H	C ₆ H ₆		2.36	2.36	
	H	CN	DME		0.66	1.09	
	Cl	CN	C ₆ H ₆		0.59		

IV.3 Discussion

It is obvious that the reaction sequence introduced in Ch. III applies to reactions of trivalent phosphorus compounds with p-quinones: highly reactive phosphinium radicals are formed and addition takes place with neutral quinone molecules.

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 (reaction IIb).

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 no equimolar amounts of quinone and phosphite were mixed.

Using TDAP, a rearrangement of the adduct radical, in

comparison with 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 rather bad in this solvent.

If the phenyl ring of the quinone is substituted by atoms other than hydrogen atoms, the formation of type 8 radicals is impossible. 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, even no radicals could be observed.

IV.4 ESR spectra and spin density calculations

Three different types of radicals are described in this section, *viz.* quinone anion radicals (4), phosphoranyl radicals (2) and β -phosphorus-substituted radicals (5, 6). For the calculation of spin densities in type 2 and 4 the following formula can be applied:

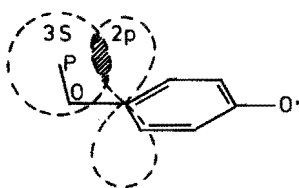
$$a^X = (S^X + \sum_i Q_{XY_i}^X) \rho_X + \sum_i Q_{Y_i X}^X \rho_{Y_i}$$

S^X covers the polarization of 1s electrons and the Q_{XY}^X and Q_{YX}^X 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 co-workers*^{5,6,7} with respect to carbon, oxygen and nitrogen. For phosphorus a value of 80 G is derived with respect to the expression $(S^P + \sum_i Q_{P_i}^P)$ from the observed ^{31}P hfs constant of PH_2 ⁸. In this radical the odd electron resides in a p_z -orbital on phosphorus and a positive sign is indicated⁹. The adjacent atom term Q_{YP}^P is set on a 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 $\text{H}_2\dot{\text{C}} - \text{PPh}_3$ ¹⁰ and PO_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: $a^X = (B_\theta + B_2 \cos^2 \theta) \rho_\pi$. B_θ 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^{1,2}. θ is the dihedral angle between the O-P bond and the axis of the p_z orbital associated with the aromatic system:



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 3s-orbitals.

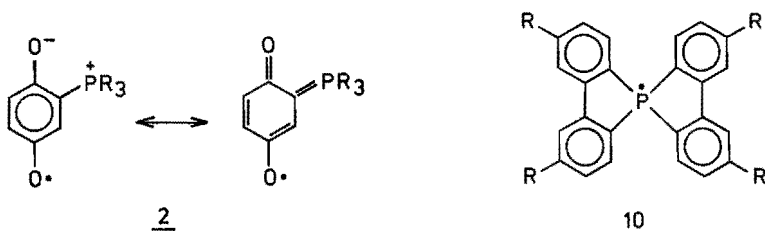
A. Quinone anion radicals

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, because they are not described in the literature in that manner. The DDQ anion radical was present in such a high concentration that ¹³C-lines were visible (see section IV.3 and Fig. 4.2). This spectrum is measured by *Kolodny and Bowers*,^{1,3}

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: $\delta_{\text{O}}=1.6$; $\delta_{\text{N}}=1.0$; $\gamma_{\text{O}}=1.2$ and $\gamma_{\text{N}}=2.0$ according to *Rieger and Fraenkel*⁷. Using the formula mentioned earlier in this section hfs constants for this radical are calculated (Table IV.3). 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 (2). These radicals are described more exhaustively in Chapter V, but introduced here as products of reactions I and IIb, according to the mechanism proposed. These radicals are resonance-stabilized as follows:



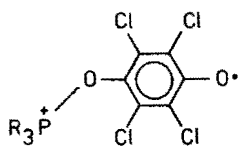
The phosphorus hfs constants are in the range of 4.5-6.5 G for monoarylsubstituted radicals (Table IV.1) and 10-20 G for symmetric bis(biphenylene)substituted radicals 10 according to *Rothuis*¹⁴. In the latter all carbon atoms attached to phosphorus possess a certain spin density which accounts for 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, $a_p=6.5$ 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). HMO-McLachlan and UHF-PPP calculations were carried out with respect to radical 2 (Table IV.4).

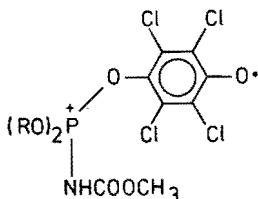
C. β -Phosphorus-substituted radicals

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 with respect to 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". 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).



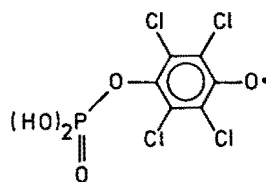
11

R= ϕ or $N(CH_3)_2$
 $a_p \approx 2.4$ G



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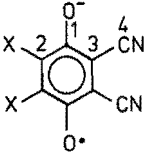
$a_p = 19.1$ G



13

$a_p = 20$ G

Table IV.3

							
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

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.

References

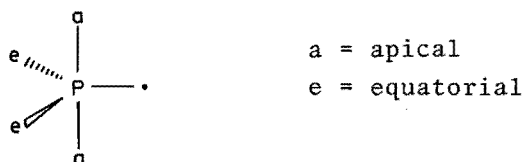
1. F. Ramirez, *Pure Appl. Chem.* 9, 337 (1964).
2. E.A.C. Lucken, *J. Chem. Soc.* 1963, 5123.
3. F. Ramirez, E.H. Chen and S. Dershowitz, *J. Amer. Chem. Soc.* 81, 4338 (1959).
4. E.A.C. Lucken, F. Ramirez, V.P. Catto, D. Rhum and S. Dershowitz, *Tetrahedron* 22, 637 (1966).
5. M. Karplus and G.K. Fraenkel, *J. Chem. Phys.* 35, 1312 (1961).
6. M.R. Das and G.K. Fraenkel, *J. Chem. Phys.* 42, 1350 (1965).
7. P.H. Rieger and G.K. Fraenkel, *J. Chem. Phys.* 37, 2795 (1962).
8. J.R. Morton, *Mol. Phys.* 5, 217 (1962).
9. T.F. Humber and M.C.R. Symons, *J. Chem. Soc. A* 1967, 1770.
10. E.A.C. Lucken and C. Mazeline, *J. Chem. Soc. A* 1967, 439.
11. S. Subramanian, M.C.R. Symons and H.W. Wardale, *J. Chem. Soc. A* 1970, 1239.
12. B. Allen and A. Bond, *J. Phys. Chem.* 68, 2439 (1964).
13. N.H. Kolodny and K.W. Bowers, *J. Amer. Chem. Soc.* 94, 1113 (1972).
14. R. Rothuis, Thesis Eindhoven (1974).

CHAPTER V

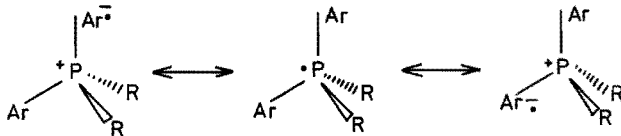
Reactions of trivalent phosphorus compounds to obtain phosphoranyl radicals

V.1 Introduction

Phosphoranyl radicals ($\dot{\text{P}}\text{R}_4$) have been extensively studied for the last ten years, both in solid matrixes and in solution. A majority of the measured radicals does possess extraordinary high phosphorus hyperfine coupling constants (700-1300 G), due to the presence of the odd electron in an equatorial ligand (sp^2 -hybridized) of a trigonal bipyramidal (TBP) configuration:



On the other hand, phosphoranyl radicals with small phosphorus hyperfine splitting constants are known, *e.g.* the radicals described in Ch. II, III and IV, as far as tetra-substituted free radicals are concerned. In these radicals the unpaired electron is able to "flee" to an aromatic substituent, resulting in a poor interaction with the nucleus of phosphorus, due to spin polarization via a P-C bond. Consequently, this type of radical must have a tetragonal coordination. According to the nomenclature even the name of this type changes from phosphoranyl radical to phosphobetaine free radical.



V.2 Trigonal bipyramidal phosphoranyl radicals

In phosphoranyl radicals having a TBP configuration the equatorial position allows the electron to interact with the nucleus of the phosphorus atom and the different values of the a_p are explained in terms of distortion of the TBP configuration. For example, *Higuchi*¹ calculated a_p 's by the MO or VB method, including the phosphorus 3d-orbitals, dependent on the bond angles in PF_4 . When comparing with the experimental values of *Fessenden et al.*² ΔF_{ap}^{PF} and ΔF_{eq}^{PF} were estimated to be 174° and 109° respectively.

Substitution of a chlorine atom by a methyl group in PCl_4 leads to a decrease in the value of a_p , too. However, *Kokosehka and Brinckman*³ ascribed this effect to the decrease in electronegativity of the methyl group with respect to chlorine. Further substitution should reduce the a_p more, which is in proper agreement with the results of different authors (Table V.1).

Table V.1

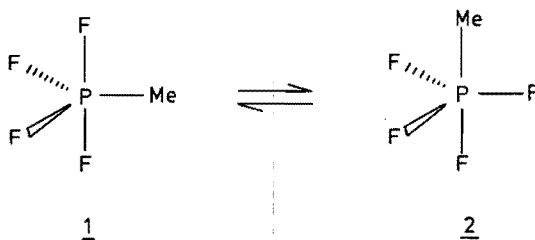
	a_p	a_{ap}	a_{eq}	Ref.
$\cdot PCl_4$	1214	$a_{Cl} = 62.5(2)$	$a_{Cl} = 7.5(2)$	3
$\cdot PCl_3Me$	1077	-	-	3
$\cdot PCl_2(Me)OBU^t$	1003	$a_{35Cl} = 30.9(2)$ $a_{37Cl} = 25.8(2)$	-	4
$\cdot PCl(Et)_2OBU^t$	794	$a_{35Cl} = 38.9(2)$ $a_{37Cl} = 32.2(1)$	-	4
$\cdot P(Me)_3OBU^t$	618.7	$a_H = 4.6(3)$	$a_H = 2.8(6)$	5

In chlorine-substituted phosphoranyl radicals two different isotropic hyperfine splitting constants can be calculated from the anisotropic ones (or measured when solutions are used). The large coupling constant is caused by two equivalent chlorine atoms in the apical positions, whereas the equatorial atoms account for the smaller one. An explanation of this rule (which can be applied to other substituents as well) is given by *Gilbro and Williams*⁶. A theoretical model is proposed here, in which the electron resides in an MO, which is represented as a Rundle three-centre non-bonding orbital. According

to this description the unpaired electron is largely distributed over the p_z - and d-orbitals of the apical ligands but not of the equatorial ones. The secondary effect is that the phosphorus hyperfine coupling constant will be more influenced by changes in electronegativity of apical substituents (see also Table V.1, in some cases different hfs-values for the two isotopes of chlorine can be described).

The validity of this model is supported by measurements of POCl_3 . From the anisotropic hyperfine splitting constants of the two apical chlorines (25-70 G), spin densities of 0.29 in each of the ligand 3p-orbitals were estimated. The isotropic phosphorus splitting of 1371 G corresponds to a spin density of 0.38 in the 3s-orbital ($Q_P^S=3640^7$; $a_P=Q_P^S \rho^S$). Thus the odd electron is largely confined to the phosphorus 3s-orbitals and p-orbitals of the apical ligands, as indicated by the sum of the spin densities in these positions (0.96).

From Table V.1 can also be seen that the most electronegative atoms tend to occupy the apical positions, *viz.* in $\text{PCl}_2(\text{Me})\text{OBu}^t$. This preference is based on the *Muetterties-rule*⁸, which has been derived from the chemistry of the penta-coordinated phosphorus compounds. The theoretical argument for this rule is that the p_z - and d-orbitals of phosphorus at the apical positions are directed in space and can provide good overlap with substituents that pull electrons away from phosphorus. On the contrary, the equatorial sp^2 -orbitals will bond best with electrons close to phosphorus, *i.e.* with substituents that are electron-donating with respect to the api-

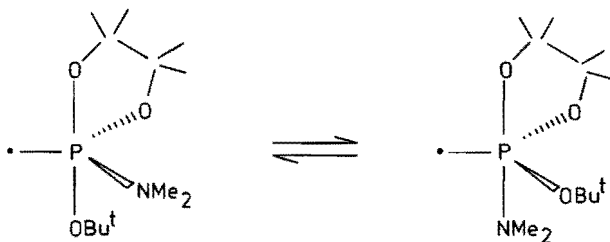


cal substituents. For example structure 1 is more stable than 2 with an energy difference of 39 kcal.mol^{-1} calculated by the CNDO/2 method, according to *Gillespie et al.*⁹.

Obviously, TBP phosphoranyl radicals do follow this rule, too, as may be concluded from the experiments and from CNDO/2 calculations, according to *van Dijk et al.*¹⁰.

¹⁹F-NMR-measurements at various temperatures have shown that stereo-isomerization will occur. At sufficient high temperatures the four fluorine atoms are equivalent and two lines due to P-F coupling are observed. This process is called pseudo-rotation and is observed in a wide variety of penta-coordinated phosphorus compounds¹¹. However, pseudo-rotation in phosphoranyl is rare, probably due to the impossibility to measure at high temperatures, because of the instability of phosphoranyl radicals. In $\cdot\text{PX}_4$, where X=H¹², F¹³ or Cl¹⁴, equivalent values for the hfs constants of the substituents are reported.

A clearer example of pseudo-rotation in phosphoranyl radicals is the stereo-isomerization of 3 and 4, due to approximately equal electronegativity of the t-butoxy and dimethylamino groups¹⁵.



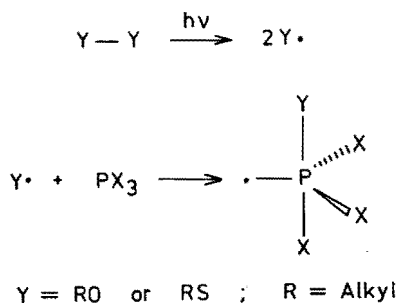
At -120°C the ESR spectrum shows the features of radical 3 ($a_p=849 \text{ G}$, $a_N=9.5 \text{ G}$), whereas at -110°C radical 4 ($a_p=784 \text{ G}$, $a_N=24 \text{ G}$) predominates. (Note the effect of the substituents on the coupling constants as described above). On increasing the temperature, line broadening indicates increasingly rapid pseudo-rotation.

V.3 Tetragonal phosphoranyl radicals

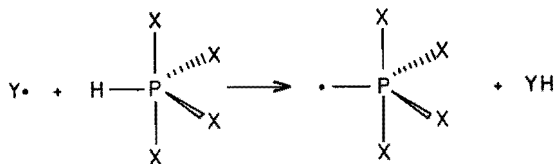
These radicals are usually called phosphobetaine free radicals. The name tetragonal phosphoranyl radical is introduced because of their strong resemblance to the "normal" phosphoranyl radicals, possessing the trigonal-bipyramidal (TBP) configuration. The tetragonal configuration (T) is characterized by a small (4.5-20 G) phosphorus hyperfine splitting constant as described in section IV.4B. Here, the odd electron is delocalized to one or more aromatic substituents. Consequently, the strong interaction of the electron with the nucleus of the phosphorus atom as in the TBP configuration is reduced to spin-polarization of the P-C σ -bond(s), while hfs constants of aromatic protons can be measured, too. Furthermore, five-coordination changes into four-coordination, because the fifth ligand has disappeared.

V.4 Preparation and stability of phosphoranyl radicals

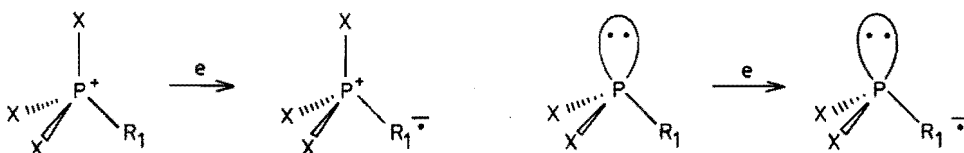
The most important method employed in preparing phosphoranyl radicals is the reaction of trivalent phosphorus compounds with photolytic generated alkoxy or thiyl radicals^{16, 17, 18}. The corresponding peroxides or disulfides are irradiated by a mercury arc in inert solvents in the presence of the phosphorus compounds.



If pentavalent phosphorus compounds are used with at least one hydrogen atom as a substituent, hydrogen atom abstraction leads to the formation of phosphoranyl radicals, too^{19,20,21}:

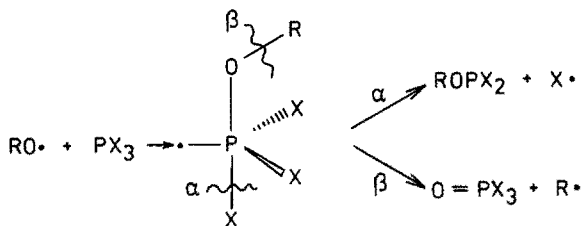


The two methods mentioned generally lead to the formation of phosphoranyl radicals having TBP-configuration, although stereo-isomerization may result in the tetrahedral configuration. However, electrolytic reduction of phosphonium ions leads exclusively to the T-configuration. These ions are tetrahedral and so are in fact trivalent phosphorus compounds in which the lone pair can be considered the fourth ligand. Obviously, electrolytic reduction of these compounds yields radicals with small a_p 's.

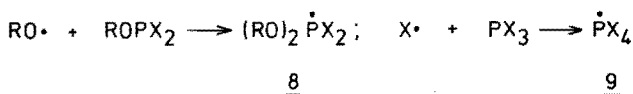


It can be seen that the latter method is employed if and only if at least one of the substituents is an aryl group where the odd electron is able to reside.

Phosphoranyl radicals in the TBP-configuration may undergo α - or β -scission reactions, according to the scheme on the next page. The kinetics of these processes have been studied thoroughly by means of ESR^{22,23} and by product studies^{24,25}. The reaction path depends on the nature of the substituents X, the solvent and the stability of the radicals X' and R'. Furthermore, other reactions will occur, *viz.* disubstituted alkoxy compounds (8) and addition products from cleaved alkyl



radicals and the parent compound (9):



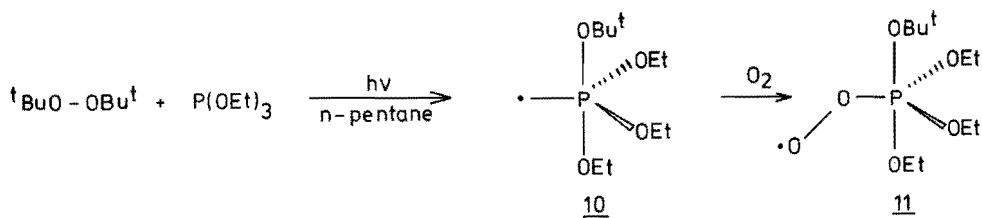
Finally, tetraalkoxyphosphoranyl radicals are able to react with molecular oxygen, yielding phosphoranylperoxy radicals with small a_p 's (± 10 G), due to a decreased interaction of the unpaired electron with the nucleus of the phosphorus atom (see section V.5).

V.5 Results

A. Irradiation experiments

According to the first method mentioned in section V.4 di-t-butylperoxide was irradiated by an UV source in order to obtain t-butoxy radicals. Reaction of these radicals with triethylphosphite in n-pentane at -50°C resulted in the formation of two different radicals. The radical with the large a_p (907 G) was formed immediately after the mercury lamp was switched on, while the one with the small a_p (9.3 G) was formed shortly afterwards (Figure 5.1). Therefore, the following reactions occurred (see Figure on next page).

Repeating the experiment, after thoroughly deoxygenation of the solution by a stream of dry nitrogen gas, only the presence of radical 10 was shown which reveals further evidence for the proposed reaction sequence.



It can be seen in Figure 5.1 that the g-value from radical 11 must be larger than the corresponding constant of 10. g is about 2.01 for various phosphoranyl radicals and 2.022 for the phosphoranylperoxy radical measured. This is in proper agreement with the corresponding value of alkylperoxy radicals (2.014-2.016), while alkoxy radicals possess g-values ranging from 2.005 to 2.010. So, the measured radical 11 is a phosphoranylperoxy radical.

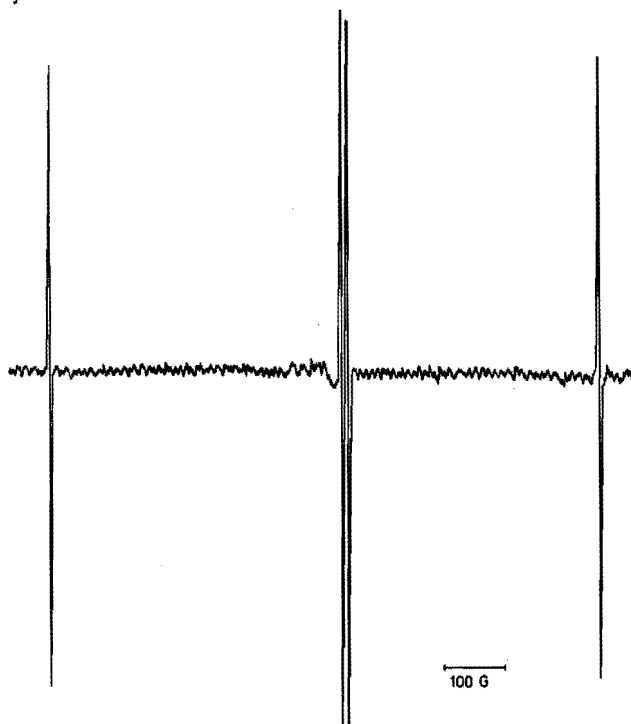
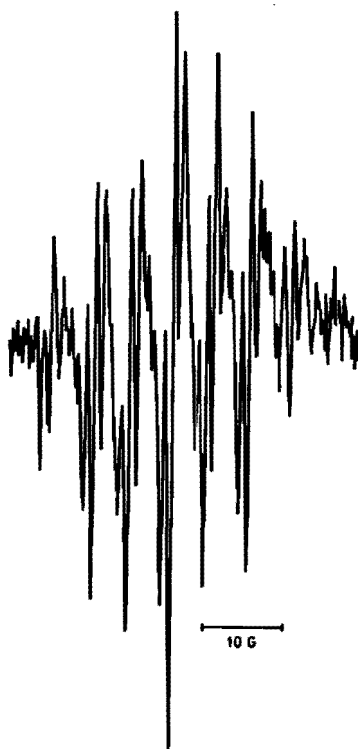
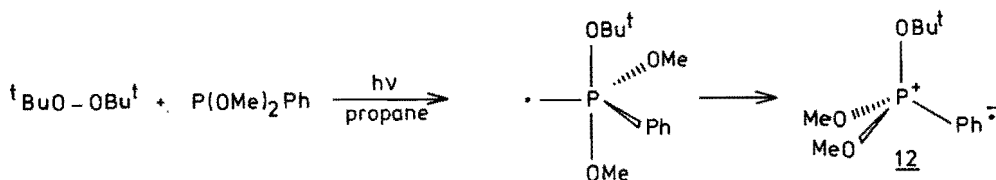


Fig. 5.1 - ESR spectrum of radicals 10 and 11, measured in propane at -80°C .

Fig. 5.2 - ESR spectrum of the tetragonally coordinated radical 12 in propane at -80°C .

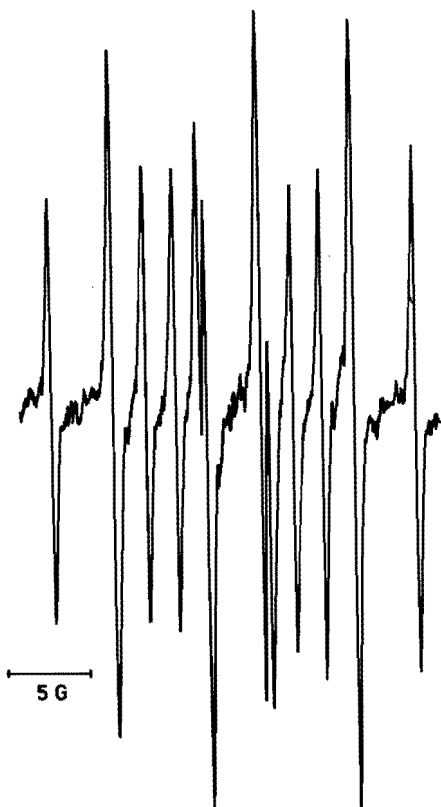


However, using dimethyl phenylphosphonite ($\text{PhP}(\text{OMe})_2$), in propane at -80°C showed an ESR-spectrum with an a_p , comparable to 11, although additional hyperfine splittings are visible (Figure 5.2). Analysis of this spectrum indicated the presence of three pairs of atoms with nuclear spin $\frac{1}{2}$. Consequently, the odd electron is delocalized over the phenyl ring and, by coincidence, a_p is equal to $a_{\text{H}}^{\text{para}}$.



The hyperfine splitting constants are 9.7 G for phosphorus and the para-substituted hydrogen atom, 5.5 G for the ortho protons and 0.9 G for the meta protons. The coincidence mentioned above is confirmed later by *Davies, Parrott and Roberts*²⁶, who measured the adduct of diethyl phenylphosphonite

Fig.5.3 - ESR spectrum of the electrolytically generated dimethylphenylphosphonite anion radical related to 12.

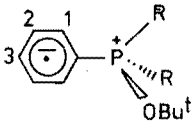
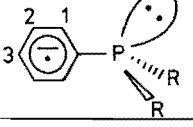
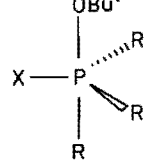


and the *t*-butoxy radical in which a_p and a_H^{para} are equal to 9.25 G with slightly different coupling constants for the other hydrogen atoms. However, substitution of ethoxy or methoxy groups by chlorine atoms leads to a phosphoranyl radical in the TBP-configuration ($a_p=1009$ G). The reason of this effect shall be explained in section V.6.

In order to get more information about the distribution of the odd electron, the phenyl ring was substituted at the para position. The reaction of the *t*-butoxy radical with di-

ethyl p-bromophenylphosphonite yielded a radical with a poorly resolved ESR spectrum (a_p of approximately 12 G) and additional splittings of ortho and meta protons.

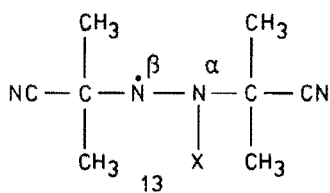
Table V.2

	<u>Solvent</u>	<u>R</u>	<u>a_p</u>	<u>a_1</u>	<u>a_2</u>	<u>a_3</u>
	propane	OMe	9.7	5.5	0.9	9.7
	propane ²⁶	OEt	9.25	5.15	1.10	9.25
	DMF	Me	9.1	3.3	0.4	8.7
	DMF	OMe	9.1	3.9	<0.1	5.9
	<u>Solvent</u>	<u>R</u>	<u>X</u>	<u>a_p</u>		
	propane	OEt	.	.	907	
	propane ²⁶	OCH ₂ CF ₃	.	.	703	
	propane	OEt	'O-O	.	9.3	

On the other hand, in a similar reaction with the p-methoxy and p-methyl substituted analogous β -scission occurred and t-butyl radicals were observed (10 lines, $a_H=22.8$ G). Using the scavenger 2-methyl-2-nitrosopropane in order to observe the intermediate phosphoranyl radicals, if any, resulted in a spectrum in which adducts of the scavenger with three scission products were recognized easily, *viz.* of t-butyl, t-butoxy and methoxy radicals (see Figure 5.4).

Using other radical precursors than di-t-butylperoxide, *viz.* disulfides and azo-(bis)isobutyronitrile (AIBN), the latter being a well-known initiator of polymerization reactions, did not gain relevant results. However, using AIBN in combination with di-t-butylperoxide, a radical with two nonequivalent nitrogen splitting constants was observed. During this unexpected reaction, AIBN seems to act as a scavenger for the short-lived radicals, created in the reaction described in Figure 5.4. The adduct radical may have the follow-

ing structure:



$$a_{\text{N}}^{\alpha} = 9.2 \text{ G}; a_{\text{N}}^{\beta} = 12.6 \text{ G} \\
 \text{X} = \text{Bu}^t, \text{OBU}^t \text{ or OEt}$$

It may be noted that the normal photolytic reaction of AIBN is yielding molecular nitrogen and 2-cyanopropyl radicals.

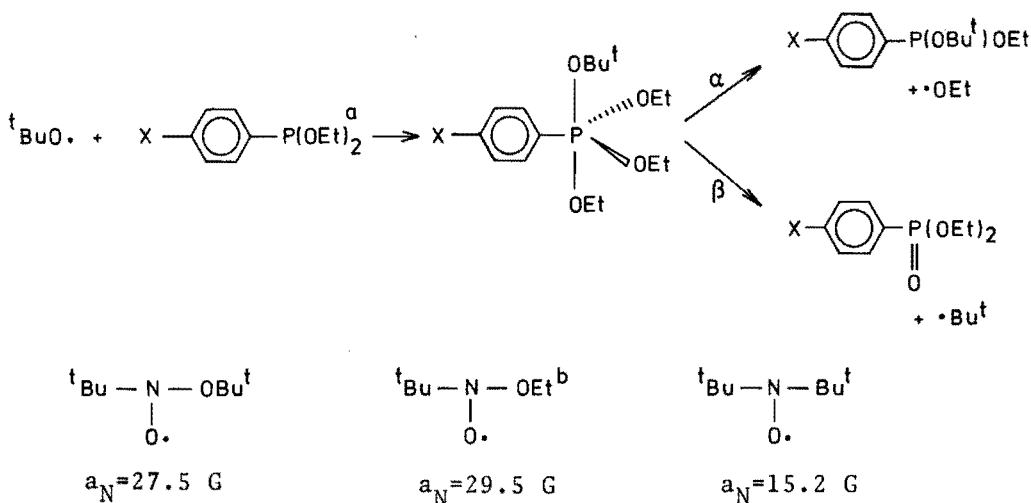


Figure 5.4 Reaction of t-butoxy radicals with aryldimethyl phosphite; spin adducts of 2-methyl-2-nitrosopropane with radicals produced in the reaction
 a. $\text{X} = \text{CH}_3$ or OCH_3
 b. *Wargon et al.* reported $a_{\text{N}} = 29.7 \text{ G}$ in methanol at -78°C

B. Electrochemical experiments

Electrolysis of trivalent phosphorus compounds, possessing at least one aryl ligand, leads to anion radicals, closely related to tetrahedral coordinated phosphoranyl radicals,

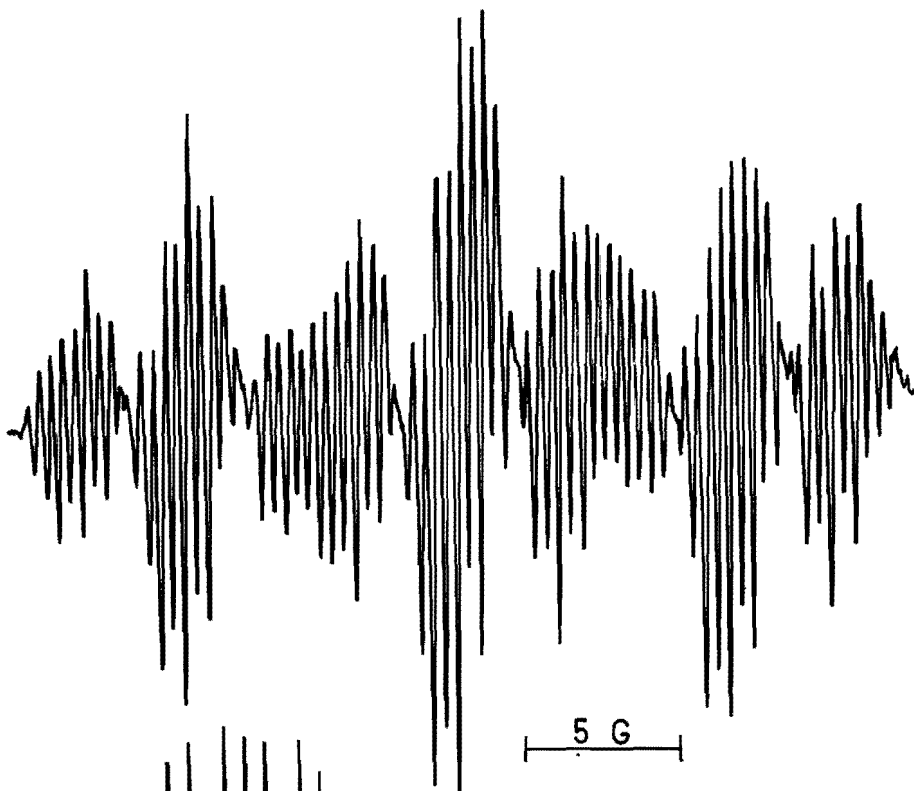


Fig.5.5 - ESR spectrum of the electrolytically generated dimethylphenylphosphine anion radical in DMF at -60°C (above). Additional methyl group splittings are visible.

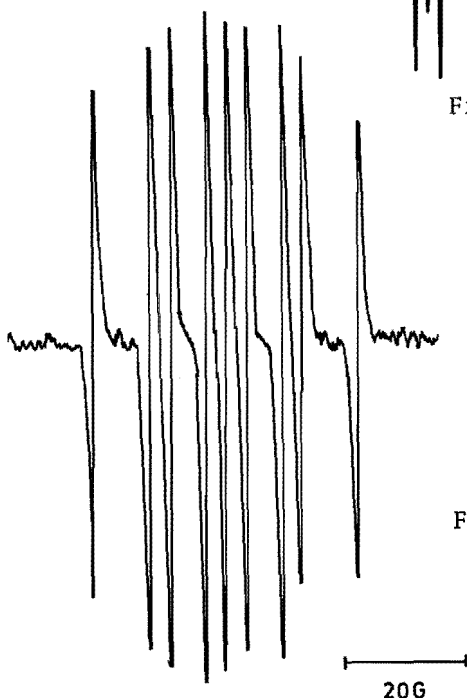


Fig.5.6 - ESR spectrum of spin adduct 13 with AIBN as the scavenger (left).

as mentioned in section V.4. According to *Gerson*²⁸, electrolytic reduction was carried out in DMF at temperatures near the freezing point of this solvent ($\pm -60^{\circ}$ C) using tetraethylammonium bromide as supporting electrolyte. On repeating the experiment of *Gerson* at -50° C spectral data (Table V.2) could be derived which confirms the relationship of the two radical types. The same method was employed to prepare the anion radicals of dimethyl phenyl phosphonite and the p-substituted analoga. The best results were obtained with the first one (Figure 5.3) and the main difference is a lower value of $a_{\text{H}}^{\text{para}}$ of 5.9 G, while the other hfs constants are about the same as in the phosphoranyl radical, although slightly smaller values for all positions were observed.

V.6 Calculations

A. Spin density calculations

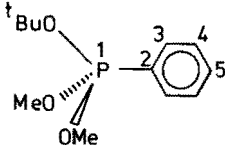
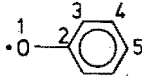
Spin density calculations with respect to phosphoranyl radicals in the TBP-configuration are not described in the literature until sofar, except for $\dot{\text{P}}\text{F}_4$ (see section V.1). However, *van Dijk*²⁹ has developed a computer program, based on the spin-projected semi-empirical UHF method of *Amos and Snyder*³⁰, including the phosphorus 3d-orbitals. This program can only be used for T-like phosphoranyl radicals. With this program radical 12 is calculated, using the parameters for the core and repulsion integrals with respect to the phosphorus and carbon atoms as described and these parameters for the methoxy group according to *van der Hout-Lodder*³¹. The phosphorus hyperfine splitting constant is dependent on the spin density of this atom as well as the spin density of the adjacent carbon atom (1).

Using $Q = -27$ G the spin densities of the other carbon atoms in the phenyl ring can be calculated by means of the *McConnell* relation: $a_{\text{H}} = |Q| \rho_{\text{C}}$. Because of the conservation of spin density (2) the sum of spin densities on phosphorus and adjacent carbon atom is calculated. Solving the two equations yield

the data given in Table V.3.

$$\left. \begin{aligned} a_P &= 80 \rho_P^\pi - 40 \rho_{C_1}^\pi & (1) \\ \rho_P^\pi + \rho_{C_1}^\pi + \sum_i \rho_{C_{ring}}^\pi &= 1 & (2) \end{aligned} \right\} a_P = 80 \left(1 - \sum_i \rho_{C_{ring}}^\pi - \rho_{C_1}^\pi \right) - 40 \rho_{C_1}^\pi$$

Table V.3

atom					
	$\rho_{exp.}^{a)}$	$\rho_{exp.}^{b)}$	$\rho_{calc.}$	$\rho_{exp.}$	$\rho_{calc.}$
1	0.179	0.196	0.136	0.266	0.198
2	0.114	0.162	0.268		0.125
3	0.204	0.191	0.222	0.251	0.253
4	-0.033	-0.041	-0.088	-0.070	-0.071
5	0.359	0.342	0.327	0.372	0.315

a) Data derived from measurements described in this work.

b) Data derived from measurements of *Davies et al.*²⁶.

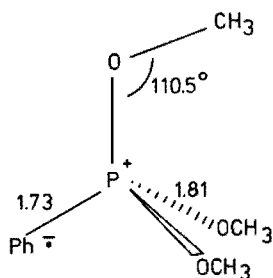
Furthermore, a good comparison can be made with the phenoxy free radical, measured by *Kochi*²² as a result of α -scission of phosphoranyl radical 12. The spectral data are related to the data derived from the phosphoranyl radical as far as the hydrogen hfs constants of the phenyl ring are concerned. This indicates a strong resemblance with respect to the electron-withdrawing effect of P⁺ and O. on the phenyl ring. On the phenoxy radical a calculation is performed according to *McLachlan* (for details see section II.4) which is in good agreement with the experimental results (see also Table V.3). The Rieger and Fraenkel parameters are $\delta_O = 1.9$ and $\gamma_{CO} = 1.6$ according to *Dimroth et al.*²³.

Finally, decreasing the value of these parameters, which

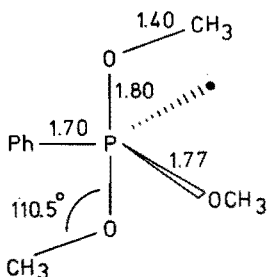
means physically that the electronegativity of the substituent is lowered, spin densities are calculated which are coming close to those measured in the electrolytically generated dimethylphenylphosphonite anion radical. The phosphorus atom in this radical ought to have a less electron-withdrawing effect on the phenyl ring than the positively charged one in the phosphoranyl radical.

B. Calculations concerning the geometry of phosphoranyl radicals

From the previous sections it is clear that the molecular geometry (TBP or T) is very important with respect to the magnitude of the phosphorus hyperfine splitting constants and *vice versa*. CNDO/2 calculations are performed with respect to distinct radicals by *van Dijk et al.*²¹. With the aid of a SIMPLEX procedure²⁶ the energetically best configuration was calculated, with optimal distances and bond angles. However, optimization for the bond angles of the phosphorus atom was not allowed because they are determined by the chosen configuration: 109° for the T-configuration and 90° and 120° for a TBP geometry. Some typical distances and bond angles for trimethylphenylphosphonite are given in Figure 5.5. Furthermore, it can be seen that the T-configuration is energetically favoured, which is in good agreement with the observed small a_p for this radical.



$E = -134.5585$ a.u.



$E = -134.5288$ a.u.

The difference in energy for the two structures is 0.0297 a.u. which is 18.6 kcal.mole⁻¹.

From the experiments of *Davies et al.*¹⁸ (see also section V.5) a remarkably increased value for the a_p is observed (9.7 to 1009 G), if the methoxy groups are substituted by chlorine, in other words, if electron-donating substituents are replaced by electron-withdrawing ones in the apical positions. Consequently, the latter ought to have TBP-geometry. This observation is confirmed by calculations where one methoxy group is replaced by the trifluoromethoxy one. The TBP-configuration of $\text{PhP}(\text{OCH}_3)_2\text{OCF}_3$ is 14.2 kcal.mole⁻¹ more favourable than the tetrahedron-like geometry. For this phosphoranyl radical a deviation of the ideal TBP-geometry is also calculated, *i.e.* the so-called square pyramidal structure where $\angle\text{OPO}$ is 109° instead of 180° (see Figure 5.5). A small difference of 0.9 kcal.mole⁻¹ in favour of the TBP-geometry indicates that a slightly distorted TBP-geometry must be borne in mind. This is in excellent agreement with calculations concerning the PF_4 radical, described in section V.2 where $\angle\text{F}_{\text{ap}}\text{PF}_{\text{ap}}$ is estimated to be 174°.

Finally, the trial structures according to *Muetterties'* rules for TBP-geometry do have the lowest energy for all the phosphoranyl radicals calculated, indicating a general application of these rules for pentavalent (non-radical) compounds as well as phosphoranyl radicals, possessing the configuration mentioned above.

V.7 Discussion and concluding remarks

From the data presented in the preceding sections it is easy to distinguish the configuration of phosphoranyl radicals which can be derived from the magnitude of the phosphorus hyperfine splitting constant. The remarkably smaller value of the a_p is due to delocalization of the unpaired electron with the aid of π -ligands, *cf.* aromatic rings, which leads to T configuration. However, some aryl-substituted phospho-

ranyl radicals do still possess TBP configuration. This is caused by the introduction of electron-withdrawing ligands, *viz.* halogen or trifluoromethyl, increasing the positive charge on the phosphorus atom. Consequently, delocalization of the odd electron from phosphorus to the aromatic system has become energetically unfavourable. CNDO/2 calculations with respect to different phenyl-substituted phosphoranyl radicals in the two configurations mentioned are in excellent agreement with the observations (see also section V.6).

Until sofar, realistic spin density calculations can be performed only with respect to tetragonal phosphoranyl radicals. The computer program, developed by *van Dijk*, based on the UHF-PPP method and including the phosphorus 3d-orbitals, gives a proper approximation of the measured a_p 's. For the TBP configuration the large value of Q for the 3s-orbital of phosphorus (3640 G) and the uncertainty about the contribution of the other s-orbitals of this atom cause large differences for the a_p if subtle changes for the spin densities are calculated.

However, the best approximation for the spin density in the 3s-orbital seems to be calculations in accordance with the INDO method, although the exponent for the wave function of the 3d-orbitals which is assumed to be constant in this method, is dependent on the effective charge of the phosphorus atom.

The addition of highly reactive radicals, such as t-butoxy radicals, always yield phosphoranyl radicals in TBP configuration first. If these radicals cannot be measured in that configuration, stereoisomerization has occurred or scission reactions have taken place or both. It has been proved by *Watts et al.*^{3*} that phenyl-substituted phosphoranyl radicals may undergo accelerated scission reactions. All scission products were measured by spin trapping and sometimes the signal of the tetragonally coordinated radical was present, too. This competition may be the reason for measuring only one radical in the T configuration *via* the TBP configuration.

References

1. J. Higuchi, *J. Chem. Phys.* 50, 1001 (1969).
2. R.W. Fessenden and R.H. Schuler, *J. Chem. Phys.* 45, 1845 (1966).
3. G.F. Kokoszka and F.E. Brinckman, *J. Amer. Chem. Soc.* 92, 1199 (1970).
4. D. Griller and B.P. Roberts, *J. Chem. Soc., Perkin II* 1973, 1339.
5. P.J. Krusic, W. Mahler and J.K. Kochi, *J. Amer. Chem. Soc.* 94, 6033 (1972).
6. T. Gillbro and F. Williams, *J. Amer. Chem. Soc.* 96, 5032 (1974).
7. P. Schipper, E.H.J.M. Jansen and H.M. Buck, *Topics in Phosphorus Chemistry*, J. Wiley & Sons (in press).
- 8a. E.L. Muettterties, W. Mahler, K.J. Packer and R. Smutzler, *Inorg. Chem.* 2, 613 (1963).
- b. E.L. Muettterties, W. Mahler and R. Smutzler, *Inorg. Chem.* 3, 1298 (1964).
9. P. Gillespie, *Angew. Chemie* 83, 691 (1971).
10. J.M.F. van Dijk, J.F.M. Pennings and H.M. Buck, *J. Amer. Chem. Soc.*
11. R.S. Berry, *J. Chem. Phys.* 32, 933 (1960).
12. C.A. McDowell, K.A.R. Mitchell and P. Raghunathan, *J. Chem. Phys.* 57, 1699 (1972).
13. J.R. Morton, *Can. J. Phys.* 41, 706 (1963).
14. A. Begum and M.C.R. Symons, *J. Chem. Soc. A* 1971, 2065.
15. R.W. Dennis and B.P. Roberts, *J. Organomet. Chem.* 47, C 8 (1973).
16. P.J. Krusic, W. Mahler and J.W. Kochi, *J. Amer. Chem. Soc.* 94, 6033 (1972).
- 17a. A.G. Davies, D. Griller and B.P. Roberts, *Angew. Chem.* 38, C 8 (1972).
- b. A.G. Davies, D. Griller and B.P. Roberts, *J. Chem. Soc., Perkin II* 1972, 993.
18. A.G. Davies, D. Griller and B.P. Roberts, *J. Organomet. Chem.* 38, C 8 (1972).
19. D. Griller and B.P. Roberts, *J. Organomet. Chem.* 42, C 47 (1972).
20. D. Griller and B.P. Roberts, *J. Chem. Soc., Perkin II* 1973, 1416.

21. R. Rothuis, Thesis Eindhoven (1974).
22. A.G. Davies, D. Griller and B.P. Roberts, J. Chem. Soc., Perkin II 1972, 2224.
23. W.G. Bentrude, J.J.L. Fu and P.E. Rogers, J. Amer. Chem. Soc. 95, 3625 (1973).
24. W.G. Bentrude, E.R. Hansen, W.A. Khan, T.B. Min and P.E. Rogers, J. Amer. Chem. Soc. 95, 2286 (1973).
25. G.B. Watts and K.U. Ingold, J. Amer. Chem. Soc. 94, 2528 (1972).
26. A.G. Davies, M.J. Parrott and B.P. Roberts, J. Chem. Soc., Chem. Comm. 1974, 27.
27. J.A. Wargon and F. Williams, J. Amer. Chem. Soc. 94, 7917 (1972).
28. F. Gerson, G. Plattner and H. Bock, Helv. Chim. Act. 53, 1629 (1970).
29. J.M.F. van Dijk, J.F.M. Pennings and H.M. Buck, J. Amer. Chem. Soc. (1975).
- 30a. T. Amos and L.C. Snyder, J. Chem. Phys. 41, 1773 (1964).
b. L.C. Snyder and T. Amos, *ibid* 42, 3670 (1965).
31. A.E. van der Hout-Lodder, Thesis Eindhoven (1972).
32. J. Kochi and P.J. Krusic, J. Amer. Chem. Soc. 95, 3626 (1973).
33. K. Dimroth, A. Berndt, F. Bär, R. Volland and A. Schweig, Angew. Chem. 79, 69 (1967).
34. G.B. Watts, D. Griller and K.U. Ingold, J. Amer. Chem. Soc. 94, 8784 (1972).

CHAPTER VI

Experimental

VI.1 Instrumental equipment

A. Hardware

The ESR spectra were recorded on a Varian E-4 spectrometer with its variable temperature auxiliary equipment. Irradiation experiments were carried out with the aid of a Philips SP 500 W lamp and electrolyses with a DC current of 10 μ A to 100 μ A using a voltage of 0-400 V. A number of spectra was punched to be processed by a computer in order to obtain a correct analysis.

The NMR spectra were recorded on a Varian A-60a or Varian T-60 spectrometer.

The UV/VIS spectra were recorded on a Perkin-Elmer 124 spectrophotometer.

Calculations have been performed on an IBM 360-75 of Philips Computer Centre or on Burroughs B6700 and a Philips P9200 Time-sharing systems of the Eindhoven University of Technology.

B. Software

ESR spectra are analyzed by means of the program ESRCON written by *J. Heinzer*¹ and simulated by a program written by *A.H. Huizer* of the University of Leiden.

Spin density calculations according to *McLachlan* were carried out on the time-sharing system. Similar calculations concerning phosphoranyl radicals in a tetrahedral configura-

tion with the aid of a program developed by *van Dijk*². CNDO and INDO calculations were carried out by means of the program CNINDO written by *P.A. Dobosh*³.

VI.2 Syntheses

Trimethylphosphite and *triethylphosphite* were commercially available (BDH) and distilled from sodium before use.

9,10-Phenanthrenequinone, *acenaphthenequinone* and *diphenylmethyl bromide* (FLUKA AG) were crystallized from benzene.

Methyl vinyl ketone (Schuchard) and *tris(dimethylamino)phosphine* were distilled before use.

p-Benzoquinone, *chloranil* and *2,3-dicyano-5,6-dichloro-p-benzoquinone* were commercially available. The former was sublimated by means of steam distillation.

Bis(2,6-dimethyl(phenyl)methyl bromide) was a gift from drs. C. Kooistra of this laboratory.

Tri(dimethylamino)phosphine

The best results were obtained by the method of *Burgada*⁴. A solution of PCl_3 (60 g, 0.44 Mol) in 750 ml dry ethoxyethane was cooled to -10°C . An excess (200 ml) of dry dimethylamine was added, maintaining the temperature below -5°C . After standing overnight the solution was filtered and washed with dry ethoxyethane. The filtrate was concentrated and distilled at $49-51^\circ \text{C}/12 \text{ mm}$. Yield 82%. PMR δ 2.5 (d).

2-methyl-2-nitrosopropane

This compound is prepared by partial oxidation from *t*-butylamine by means of hydrogen peroxide and catalyzed by sodium tungstate according to *Stowell*⁵. A solution of *t*-butylamine (18.3 g, 0.25 Mol) and 2.0 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 25 ml water was cooled in an ice bath. Hydrogen peroxide was added dropwise at $15-20^\circ \text{C}$ with stirring. About 1.5 g NaCl was added to break the emulsion and the blue organic layer separated, washed with dilute HCl and dried with MgSO_4 . Distillation gave 4.5 g of the blue nitroso compound which associates to

a colourless dimer when cooled in an ice bath. Yield 20%, mp 74-75^o C.

Bis-(p-nitrophenyl)methyl bromide

This compound was prepared from diphenylmethane in two steps. Firstly, 80 g of the latter was added dropwise to 280 ml fuming nitric acid, while the temperature was maintained between 20 and 25^o C. After 15 minutes at room temperature the mixture was poured in 2 l water, filtrated, washed with NaHCO₃-solution and ethoxyethane and crystallized from benzene. Yield 17%, mp 183-185^o C.

A solution of this compound (10.4 g, 0.04 Mol), N-bromosuccinimide⁵ (6.2 g, 0.042 Mol) and 0.54 g dibenzoylperoxide in 82.5 ml CCl₄/CHCl₃ (10:1) was refluxed for two hours. After filtration of the yellow succinimide the solvent was evaporated and the residue crystallized from CCl₄. Yield 24%, mp 88-90^o C. PMR δ 6.37 (H,s), δ 7.91 (phenyl,q).

2,7-Dinitrofluorenyl bromide

2,7-Dinitrofluorene (5.2 g, 0.02 Mol), 3.5 g N-Bromosuccinimide (3.5 g, 0.024 Mol) and 0.27 g benzoylperoxide were dissolved in nitrobenzene. The solution was refluxed for half an hour, cooled and a brown solid was separated. Crystallization from propanon gave 1 g of the product. Yield 16%, mp 267.5-268.5. PMR δ 6.53 (H,s), δ 8.26 (arom.,m).

Dinitrophenanthrenequinone⁶

A solution of 9,10-phenanthrenequinone (30 g, 0.14 Mol) in 400 ml fuming nitric acid and 50 ml concentrated sulfuric acid is boiled during 45 minutes. The mixture is poured in 3.6 l water. The washed solid was brought in ethanol and refluxed in order to remove other substitution products. The insoluble yellow product was filtrated and crystallized from glacial acetic acid. Yield 80%, mp 303-304^o C.

3,4-Dinitroacenaphthenequinone⁷

10 g Acenaphthenequinone was dissolved in 150 ml concentrated sulfuric acid. This compound is nitrated by adding a

mixture of 7 ml nitric acid ($d=1.51$) and 20 ml sulfuric acid. The mixture is heated to 80° C and poured on ice. The filtrate is washed by dilute Na_2CO_3 and crystallized from glacial acetic acid. Mp $> 300^{\circ}$ C.

*3-Benzylideneacetylacetone*⁸

Benzaldehyde (10.6 g, 0.1 Mol) and acetylacetone (10.0 g, 0.1 Mol) were mixed and cooled to -10° C. 1 ml piperidine was added dropwise during a few minutes and the reaction was allowed to proceed at 0° C for three days. The mixture was diluted with ether and washed with dilute HCl, dilute NaOH and water respectively. The ethoxyethane was removed and the product isolated by distillation (bp 168° - 170° C/13 mm). Yield 66%.

2,3-Dicyano-p-benzoquinone

2,3-Dicyanohydroquinone was prepared according to *Hefferich*⁹ from benzoquinone and potassiumcyanide. This compound was oxidated by N_2O_4 ¹⁰. A mixture of fuming nitric acid (83 ml), concentrated sulfuric acid (33 ml) and As_2O_3 (100 g) is distilled slowly. The red vapour is condensated in an ice bath. 6 ml of this liquid is slowly added to a suspension of the hydroquinone (20 g, 0.125 Mol) in 300 ml CCl_4 . The mixture is stirred for five minutes and the product filtrated and crystallized from CHCl_3 /benzene. Yield 92%, mp 178° - 180° C. Element analysis: calc. C 60.67, H 1.27, N 17.72; found C 60.22, H 1.45, N 17.99.

*Dimethylphenylphosphonite*¹¹

To a solution of methanol (32 g, 1 Mol) and N,N-dimethylaniline (90 g, 0.75 Mol) in 250 ml dry ethoxyethane, phenyldichlorophosphine (90 g, 0.5 Mol) was added during one hour. The reaction was carried out in a nitrogen atmosphere and after refluxing for one hour the solution was allowed to stand overnight. A white solid was filtrated and washed with several portions ethoxyethane. The solvent was evaporated and the product distilled over a Vigreux column (bp

94.5⁰ C/13 mm). Yield 55%. PMR δ 3.6 (CH₃,d), δ 7.6 (phenyl, m).

Dimethylanisylphosphonite

A mixture of methanol (15.4 g, 0.48 Mol) and 48.6 g triethylamine (48.6 g, 0.48 Mol) in 100 ml dry pentane was added dropwise to p-anisylchlorophosphine (50 g, 0.24 Mol) prepared according to *Bentrude*¹² in 200 ml ice-cold pentane. The solution was refluxed for half an hour and a white residue filtrated. The pentane was removed and the residue distilled (bp 75-76⁰ C/0.1 mm). Yield 30%. PMR δ 3.6 (CH₃,d), δ 3.8 (OCH₃,s), δ 7.0 and 7.6 (C₆H₄,q).

References

1. Quantum Chemistry Program Exchange, Indiana University, U.S.A., program 197.
2. J.M.F. van Dijk, J.F.M. Pennings and H.M. Buck, *J. Amer. Chem. Soc.* 97, in press.
3. Quantum Chemistry Program Exchange, Indiana University, U.S.A., program 141.
4. R. Burgada, *Ann. Chim. France* 8, 348 (1963).
5. A.I. Vogel, *Practical Chemistry*, p. 927.
6. J. Schmidt, *Ber.* 35, 3122 (1902); *Beilstein*, VII, 807.
7. F.M. Rowe and J.S.H. Davies, *J. Chem. Soc.* 117, 1344 (1920).
8. M.E. McEntee and A.R. Pinder, *J. Chem. Soc.* 1957, 4426.
9. B. Helferich and H.G. Bodenbender, *Ber.* 56, 1113 (1923).
10. A.G. Brook, *J. Chem. Soc.* 1952, 5040.
11. D.M. Coyne, W.E. McEwen and C.A. Vandenwerf, *J. Amer. Chem. Soc.* 73, 755 (1951).
12. W.G. Bentrude, J.-J.L. Fu and P.E. Rogers, *J. Amer. Chem. Soc.* 95, 3626 (1973).

Summary

According to the investigations described in this thesis, a number of reactions of trivalent phosphorus compounds appear to be radical reactions. This especially holds good for the addition reactions where the coordination number of phosphorus is extended to four or five.

In the corresponding literature only the reactions of trivalent phosphorus compounds with alkoxy or thiyl radicals are given a clear description during which process phosphoranyl radicals ($\dot{P}R_4$) are formed having a trigonal bipyramidal geometry.

Also thanks to the extremely useful spin-trapping technique, it appeared to be possible to develop a radical mechanism for a number of reaction types, which not only explains the formation of all the reactions products and intermediates but also gives a better insight into the course of these reactions, *i.e.* the existence of an ionic mechanism, as was supposed by various authors, is improbable.

In the reactions, described in chapter II, where the strongly nucleophilic tris(dimethylamino)phosphine reacts with various aromatic bromides, three possible routes can be followed, depending on the choice of the solvent. From the products formed by these reactions may be concluded that the reaction proceeds *via* a homolytic cleavage of the C-Br bond and a heterolytic cleavage taking place with formation of both carbenium ions and carban ions. Special attention will be given to the radicals produced by this homolytic dissociation.

In the next two chapters the reactions of trivalent phosphorus compounds with aromatic carbonyl compounds are described. Essential in this case are the reducing properties of the former group of compounds, causing an electron transfer to the latter, initiating the reaction. It will be shown that it is

a three-step mechanism that leads to the formation of the final products. An additional argument for this mechanism is the appearance and demonstration of other radicals, *e.g.* alkyl radicals, enabling the formation of by-products. Due to the formation of the various intermediate products, some interesting ESR spectra are recorded at the same time.

The structure of phosphoranyl radicals has been described exhaustively before. These radicals may exist in two configurations, *viz.* the trigonal bipyramidal, being characterized by a very large phosphorus hyperfine splitting constant (700-1400 Gauss) and the tetragonal one, for which relatively small splitting constants are measured. It will be shown that the four-coordinated phosphoranyl radicals may be formed from the five-coordinated *via* an electron transfer from an equatorial ligand to an aromatic substituent. This will be supported by means of CNDO/2 calculations. The measurements with respect to these stereoisomerizations, however, are often hindered by scission of the phosphoranyl radicals, during which the resulting products may be shown by means of spin trapping.

Samenvatting

Volgens het in dit proefschrift beschreven onderzoek blijken een aantal reacties van driewaardige fosforverbindingen radicaalreacties te zijn. Dit geldt met name voor additie-reacties waarbij het coördinatiegetal van fosfor uitgebreid wordt tot vier of vijf.

In de corresponderende literatuur worden slechts de reacties van driewaardige fosforverbindingen met alkoxy of thiyl radicalen duidelijk beschreven waarbij fosforanyl radicalen (PR_4) ontstaan die een trigonaal bipyramidale geometrie hebben.

Het bleek mogelijk, mede dankzij de uiterst nuttige techniek van het vangen van zeer kort levende radicalen, voor een aantal reactietypen een radicaalmechanisme op te stellen hetwelk niet alleen de vorming van alle reactieprodukten en intermediairen verklaart, maar tevens een beter inzicht verschaft in het verloop van deze reacties, d.w.z. dat een iono-geen mechanisme, zoals verondersteld door verschillende auteurs, onwaarschijnlijk is.

In de reacties die beschreven worden in hoofdstuk II, waarbij het sterk nucleofiele tris(dimethylamino)phosphine reageert met verschillende aromatische bromiden, kunnen drie mogelijke routes gevolgd worden, afhankelijk van de keuze van het oplosmiddel. Uit de gevormde produkten van deze reacties kan worden vastgesteld, dat de reactie verloopt via een homolytische splitsing van de C-Br binding en een heterolytische splitsing, die plaatsvindt onder vorming van zowel carbeniumionen als carbanionen.

Speciale aandacht wordt gegeven aan de radicalen die ontstaan bij de homolytische dissociatie.

In de twee volgende hoofdstukken worden de reacties be-

schreven van driewaardige fosforverbindingen met aromatische carbonyl verbindingen. Essentieel is hierbij het reducerende karakter van de eerste groep van stoffen, waarbij een electron overgedragen wordt naar de laatstgenoemde, waardoor de reactie op gang wordt gebracht. Geconstateerd wordt, dat een driestaps mechanisme leidt tot de vorming van de eindprodukten. Een extra argument voor dit mechanisme is het verschijnen en aantonen van andere radicalen, b.v. alkyl radicalen, die de vorming van nevenprodukten mogelijk maken. Als gevolg van het ontstaan van de verschillende tussenprodukten, konden tevens enkele interessante ESR spectra worden opgenomen.

De structuur van fosforanyl radicalen is uitgebreid in de literatuur beschreven. Deze radicalen kunnen in twee configuraties voorkomen, te weten de trigonaal bipyramidale, die gekarakteriseerd wordt door een zeer hoge fosfor hyperfijnsplitsingskonstante (700-1400 Gauss) en de tetragonale, waarvoor relatief lage splitsingskonstanten gemeten worden. Aangetoond kan worden, dat de vier gecoördineerde fosfor radicalen kunnen ontstaan uit de vijf gecoördineerde radicalen via een electronoverdracht vanuit een equatoriale ligande naar een aromatische substituent. Dit wordt ondersteund met behulp van CNDO/2 berekeningen. De metingen met betrekking tot deze stereoisomerisaties worden echter vaak bemoeilijkt door het optreden van ontleding der fosforanylradicalen, waarbij de ontledingsprodukten door middel van spin trapping aangetoond konden worden.

Curriculum vitae

De auteur werd geboren op 14 februari 1946 te 's-Gravenzande. Na het behalen van het einddiploma HBS-b aan het 2e VCL te Den Haag werd in september 1963 begonnen met de studie in de scheikunde aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen (F-richting) werd in 1967 afgelegd. In oktober 1970 werd het doctoraalexamen afgelegd met als hoofdvak Theoretische Organische Chemie (prof. dr. L.J. Oosterhof) en als bijvakken Numerieke Wiskunde (prof. dr. G. Zoutendijk) en Radiochemie (prof. dr. E. Havinga). Gedurende de periode 1969-1970 werd een assistentschap vervuld bij de afdeling Theoretische Organische Chemie.

Medio maart 1971 werd begonnen met het onderzoek, dat in dit proefschrift beschreven is. Dit werk werd gecombineerd vanaf augustus 1971 met een functie als leraar scheikunde aan de volgende scholen: het Tilburgs Avondcollege, de R.K. Paedagogische Akademie te Schijndel, de R.K. Paedagogische Akademie Hemelrijken te Eindhoven, de Akademie voor Industriële Vormgeving te Eindhoven en het Lyceum Augustinianum te Eindhoven.

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STELLINGEN

1
Het verdient aanbeveling om na voltooiing van Zuiderzee- en Deltawerken de export van know-how en arbeid te bevorderen naar buurlanden ten behoeve van recreatieve doeleinden.

2
Het is op zijn minst voorbarig nieuwe schooltypen naar Amerikaans model te introduceren alvorens de resultaten van de mammoetwet voldoende uitgekristalliseerd zijn.

3
Het is geen stijl bij de instelling van provincies-nieuw-stijl de gemeenten over de rand van een steile afgrond te laten vallen door hun alle niet geheel onbelangrijke taken te ontnemen.

4
De conclusie van de consumentenbond, dat alkalische batterijen gebruikt kunnen worden in plaats van normale (Leclanché) batterijen, is gevaarlijk, gelet op het hoge kwikgehalte van eerstgenoemde.

Consumentengids 23, 320 (1975)

5
Het mechanisme van de reactie tussen driewaardige fosforverbindingen en α -diketonen, zoals voorgesteld door *Ogata* en *Yamashita*, is onjuist.

Dit proefschrift

6
Vele sigmatrope omleggingen worden bepaald door de op één na
hoogst bezette MO in plaats van door de hoogst bezette MO.

R.G. Woodward en R. Hoffman, *The conversation
of orbital symmetry*, Verlag Chemie 1971

7
De door *Paquette et al.* gepresenteerde ^{13}C en ^1H NMR spectra
vormen geen bewijs voor het bestaan van het 2-methylbicyclo-
(3,2,2)nonatrienyl kation.

A. Paquette, M. Oku, W.B. Farnham, G.A. Olah
en G. Liang, *J. Org. Chem.* 40, 700 (1975)

8
Het mechanisme voor de hydrolyse van dinucleosidefosfaten,
zoals voorgesteld door *Libscomb*, houdt geen rekening met de
grote stereospecificiteit van deze omzetting.

W.N. Libscomb, *Chem. Soc. Rev.* 1, 319 (1972)

9
De structuur van het tussenprodukt bij de synthese van
rheïne-1-mononucleoside, zoals voorgesteld door *Struyf*, is
onjuist.

E. Struyf, *Pharm. Weekblad* 110, 401 (1975)

10
De geometrie van het fenyl kation zoals berekend door *Swain
et al.* met behulp van de INDO methode is niet in overeen-
stemming met de resultaten van MINDO en ab initio bereke-
ningen.

C.G. Swain, J.E. Sheats, D.G. Gorenstein en
K.G. Harbison, *J. Amer. Chem. Soc.* 97, 791
(1975)