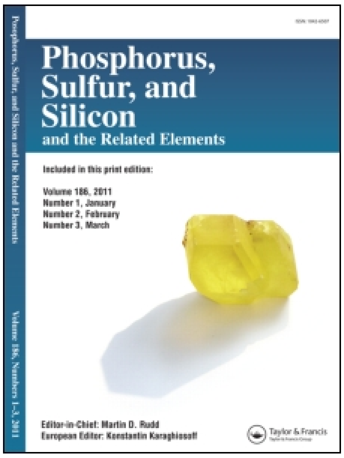


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

INTRAMOLECULAR ELECTRON TRANSFER IN PHOSPHORANYL RADICALS. AN E.S.R. STUDY ON THE STEREOISOMERIZATION OF PHENYLPHOSPHORANYL RADICALS IN SOLUTION

A. E. H. de Keijzer[a]; H. M. Buck[a]
[a] Contribution of the Department of Organic Chemistry, Eindhoven University of Technology, MB Eindhoven, The Netherlands

To cite this Article de Keijzer, A. E. H. and Buck, H. M.(1989) 'INTRAMOLECULAR ELECTRON TRANSFER IN PHOSPHORANYL RADICALS. AN E.S.R. STUDY ON THE STEREOISOMERIZATION OF PHENYLPHOSPHORANYL RADICALS IN SOLUTION', Phosphorus, Sulfur, and Silicon and the Related Elements, 42: 3, 201 — 210

To link to this Article: DOI: 10.1080/10426508908054896

URL: http://dx.doi.org/10.1080/10426508908054896

Phosphorus, Sulfur, and Silicon, 1989, Vol. 42, pp. 201–210
Reprints available directly from the publisher
Photocopying permitted by license only

ELECTRON SPIN RESONANCE STUDY OF PHOSPHORANYL RADICALS. PART II.[†] INTRAMOLECULAR ELECTRON TRANSFER IN PHOSPHORANYL RADICALS. AN E.S.R. STUDY ON THE STEREOISOMERIZATION OF PHENYLPHOSPHORANYL RADICALS IN SOLUTION

A. E. H. DE KEIJZER and H. M. BUCK

Contribution of the Department of Organic Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands.

(Received June 28, 1988; in final form August 18, 1988)

An electron spin resonance study on a series of phenylphosphoranyl radicals generated either by u.v. irradiation of solutions containing the corresponding P(III) or P(V) compounds and a dialkylperoxide, or by electrochemical reduction of the phosphonium salts, is reported. It is demonstrated, by careful examination of the phenylphosphoranyl radicals formed, that the initial precursor structure strongly defines the ultimate structure of the radicals detected. Furthermore, the transformation of a trigonal bipyramidal phenylphosphoranyl radical into its tetrahedral counterpart could actually be observed for the first time. This study therefore provides the prerequisites necessary for the isomerization process to take place.

Key words: Phosphoranyl radicals; stereoisomerization; ESR study; radical structure; TBP-e phenylphosphoranyl radicals; intramolecular electron transfer.

INTRODUCTION

During the past decade, the generation of phosphoranyl radicals in solution has been the topic of many ESR studies. A variety of phosphoranyl radicals has been generated, mostly by homolytic addition of alkyl, thiyl or alkoxy-radicals to phosphorus(III) compounds.[1]

The structure and electronic configuration of the phosphoranyl radicals studied seemed markedly dependent on the nature of the ligands around the central phosphorus atom. Usually, the structure of the phosphoranyl radicals has been discussed in terms of a distorted trigonal bipyramidal configuration in which the unpaired electron occupies an equatorial position (TBP-e). There are, however, several known examples of radicals in which the unpaired electron is centered on one of the ligands rather than on the central phosphorus atom.[2] As an important example of radicals displaying both types of radical structures, the phenylphosphoranyl radicals should be mentioned.

From previous studies[3] it was concluded that there are two general types of

---

[†] For part I, see: A. E. H. de Keijzer, H. M. Buck, *Phosphorus and Sulfur*, **31**, 203 (1987).

FIGURE 1 Phenylphosphoranyl radicals in a TBP-e (**A**) and tetrahedral (**B**) configuration.

phenylphosphoranyl radicals with the unpaired electron centered either mainly on the phosphorus atom, or on the phenyl ring (types A, and B, see Figure 1). It has been suggested[4] that, in general, all the reactions of P(III) compounds with e.g. alkoxy radicals proceed via the TBP phosphoranyl radical, but that in case phenyl ligands are present a delocalization of the unpaired electron into the phenyl ring may occur (see Figure 2). It appears that electron withdrawing ligands favour the formation of the intermediate TBP radicals, whilst substituents which are capable of inductive or conjugative stabilization of a positive charge on phosphorus favour the tetrahedral structure. Until now it has been virtually impossible, even by laser flash photolysis using a detection system capable of nanosecond response,[5] to monitor the direct chemical transformation of the intermediate TBP radical to a tetrahedral structure.

In this paper an ESR study on several phosphorus model compounds is reported, which will allow the determination of the correct prerequisites necessary to observe the actual transformation.

RESULTS AND DISCUSSION

Selected Model Compounds

Recent observations by Hamerlinck *et al.*,[6] regarding the dependence of the ultimate radical structure on the type of radical precursor used, were chosen as a starting point for the present study. In their work they demonstrated that the photolysis of compound **1** (see Figure 3) in the presence of di-t-butylperoxide yields phosphoranyl radicals with an a(P) of 65.2 mT, while no further hyperfine splittings were observed. The magnitude of the phosphorus splitting, together with the TBP structure of the precursor phosphorane, urged them to characterize the structure of the phosphoranyl radical as TBP-e, with the unpaired electron located on phosphorus in an equatorial position (**1'**).

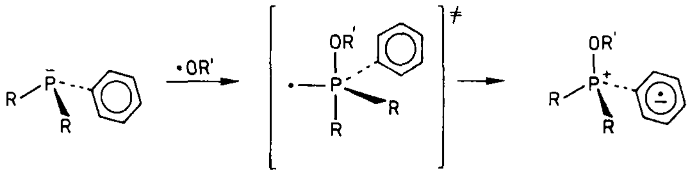


FIGURE 2 Isomerization pathway for phenylphosphoranyl radicals.

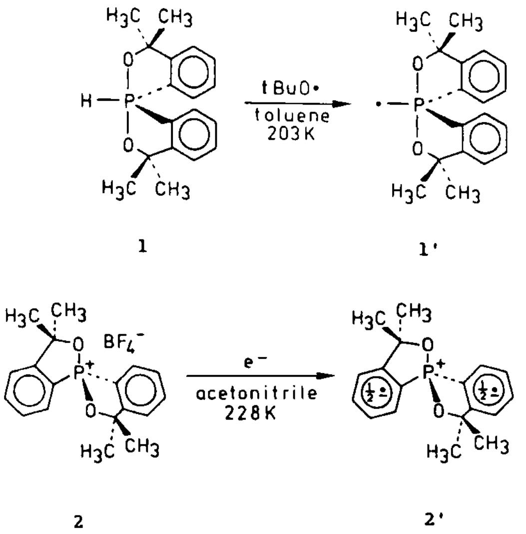


FIGURE 3 Formation of TBP-e and tetrahedral phenylphosphoranyl radicals in solution, according to Hamerlinck *et al.*[6]

Cathodic reduction of the corresponding tetrahedral phosphonium salt **2** in acetonitrile solution afforded radicals exhibiting an isotropic ESR spectrum with a low hyperfine coupling to phosphorus and a significant hyperfine coupling to the aromatic hydrogens, indicating that the unpaired electron is mainly located in the phenyl rings, with phosphorus in a tetrahedral configuration (**2'**).

Interestingly, however, a transformation of the TBP-e radical **1'** to the tetrahedral radical **2'** could *not* be induced. The behaviour of **1'** is therefore in sharp contrast with the analogous acylic radicals[3d] possessing iso-electronic ligands. These radical species show a low *a*(P) value with the unpaired electron located on the phenyl rings. The main reason for the anomalous behaviour of **1'** is probably the incorporation of a considerable amount of rigidity into the precursor phosphorane **1**. As a result, the corresponding TBP-e radical **1'** is stabilized by the equatorial-axial alignment of both benzoxa-moieties, which reduces the ring-strain in the five-membered rings, together with the preferred axial and equatorial positioning of the oxygen and carbon atoms respectively. On the basis of these observations several phosphorus model systems were prepared. In these compounds the impact of these stabilizing factors is partially reduced, therefore allowing the isomerization to a tetrahedral radical to take place. The model compounds are summarized in Figure 4. Compound **3** was selected in order to determine the influence of the axially located oxygens on the radical stability, by replacing them by less electro-negative carbon atoms. In compound **6** the influence of the rigidity of the two benzoxaphosphole moieties was reduced by replacing one of them by a more flexible dioxaphospholane ring.[7] Compounds **4**, **5** and **7** were used as the tetrahedral analogues of these compounds. Careful examination of the radicals derived from compounds **3–7** made it possible to draw some conclusions about the driving force behind the isomerization process of phenylphosphoranyl radicals.

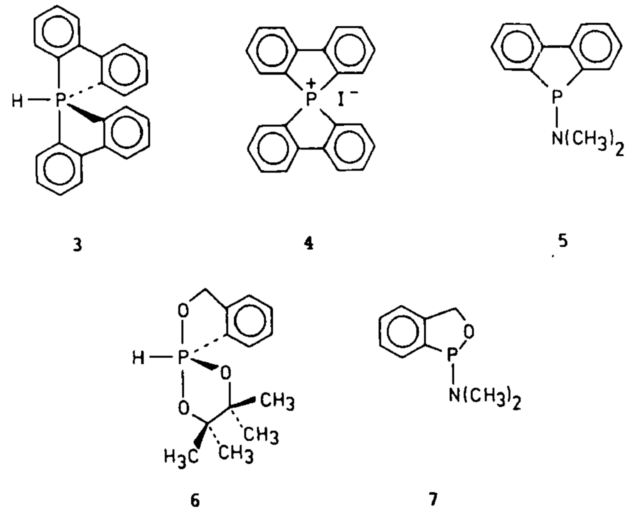


FIGURE 4 Model compounds **3–7** studied in the present work.

Photolysis and Radicals Analysis

The phosphoranyl radicals described in this paper, were produced directly in the cavity of the ESR spectrometer by employing the following methods:

a) Addition of photochemically generated t-butoxy radicals to the appropriate trivalent phosphorus compounds (**5** and **7**), usually in toluene as solvent.

b) Homolytic abstraction of the weakly bonded P–H hydrogen from five coordinated TBP phosphoranes (**3** and **6**), by means of photochemically produced t-butoxy radicals.

c) Electrochemical reduction of the corresponding phosphonium salt (**4**), usually in DMF/THF solvent.

The ESR parameters for compounds **3–7** are collected in Table I.

TABLE I

ESR parameters for the phosphoranyl radicals derived from model compounds **3–7**.

Compound[a]	**3**	**4**	**5**	**6**[d]	**6**[d]	**7**
T/°C	−60	−30	−60	−60	−60	−60
a(P)[b]	1.94	1.48	1.00	76.6	1.62	1.62
a(o-H)[b]	—[c]	0.17	0.11	—	0.87	0.87
a(m-H)[b]	—[c]	0.09	—[c]	—	0.16	0.16
a(p-H)[b]	—[c]	0.26	0.38	—	1.56	1.56
a(CH_2)[b]	—	—	—	1.1	0.54	0.54

[a] Solvent toluene except **4** DMF/THF (1 : 1). [b] All a-values in mT, all g-factors were 2.003 ± 0.001. [c] Hyperfine splittings were not resolved. [d] The initially formed radicals **6**′ are TBP-e radicals, the secondary radicals **6**″ are tetrahedral and are identical with those reported for compound **7**.

Compounds **3–5**

The radicals generated from these compounds all showed the features of tetrahedral phenylphosphoranyl radicals.[8] In the radicals derived from compound **3** a doublet splitting of 1.94 mT to phosphorus was found while no further hyperfine splitting could be observed. Electrochemical reduction of the corresponding phosphonium salt **4** resulted in a similar ESR spectrum with an a(P) of 1.48 mT and a well-observable hydrogen hyperfine splitting pattern. Couplings of 0.09 mT (4H), 0.17 mT (2H) and 0.26 mT (2H) were observed, indicating that the unpaired electron is mainly located in one of the biphenyl moieties. These observations are in excellent agreement with the data reported by Rothuis *et al.*[9]

Comparison of the ESR spectrum of the radicals generated from compound **5** with the spectra obtained for compounds **3** and **4**, revealed similar features. After computer simulation of the experimental spectrum, the following hyperfine couplings were determined: $a(\mathrm{P}) = 1.00$ mT, $a(p\text{-H}) = 0.38$ mT (2H) and $a(o\text{-H}) = 0.11$ mT (2H). The coupling to the m-H's was not resolved. From the experiment with compound **5** we are able to conclude that this type of P(III) compound is also an excellent starting compound for the generation of the desired tetrahedral phenylphosphoranyl radicals. All spectral properties mentioned above for compounds **3–5**, are typical for the tetrahedral phenylphosphoranyl radical species.

Compounds **6** *and* **7**

Upon generating phosphoranyl radicals from compound **6**, an interesting phenomenon was observed. *Two* different radical species could be detected. One radical, present immediately after commencing photolysis, shows an a(P) of 76.6 mT and an a(H) of 1.1 mT (1H), indicating the presence of a TBP-e radical structure (type A). The other radical, which shows intense multi-line resonances in the center-field region, appears to be a secondary product since its concentration increases with the duration of the photolysis.[10] The magnitude of the phosphorus splitting and the presence of well-observable hyperfine splittings to the aromatic hydrogens are typical for a tetrahedral radical species (type B). A representative spectrum, recorded at −60°C, in which both types of radicals are present is displayed in Figure 5. Radicals derived from compound **7** (see Figure 6) only gave rise to an ESR spectrum identical to the one found for the secondary radicals derived from compound **6** after prolonged photolysis, indicating the presence of tetrahedral phenylphosphoranyl radical species only.

Assignment of the Hydrogen Hyperfine Structure

TBP-e Radicals. In case of the initial detected TBP radicals derived from compound **6**, a large hyperfine splitting (1.1 mT) of only one of the $POCH_2$-hydrogens has been detected. This is consistent with the results presented by Cooper *et al.*[11] In their work they have determined the hyperfine splittings of a

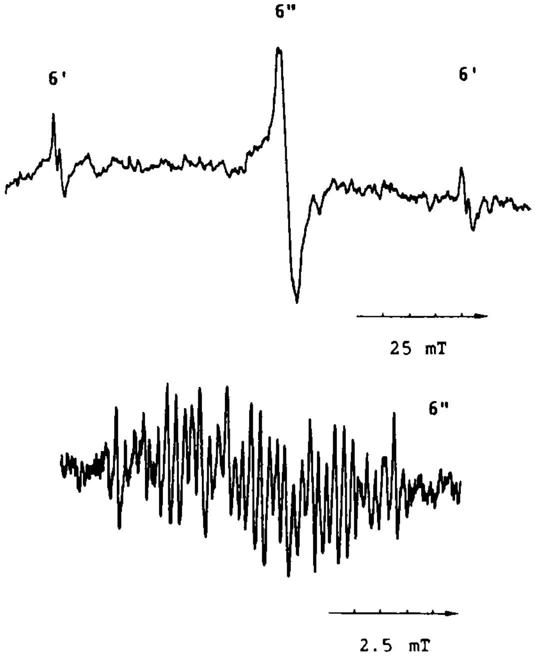


FIGURE 5 ESR Spectrum of radicals derived from compound **6** after prolonged photolysis, showing both types of radical species **6**′ (type **A**) and **6**″ (type **B**) present (upper trace) and a centerfield expansion plot of the tetrahedral radical species **6**″ (lower trace).

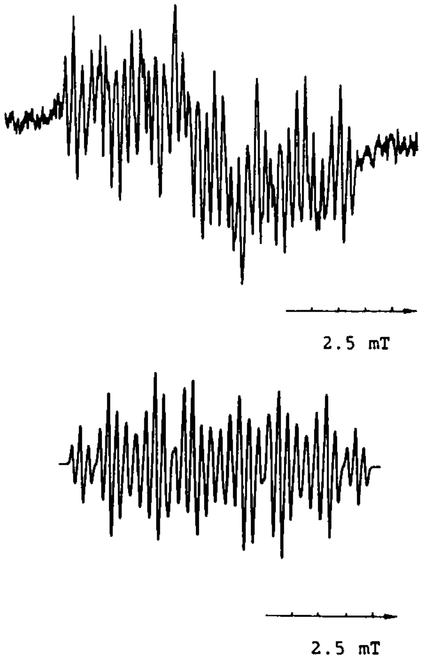
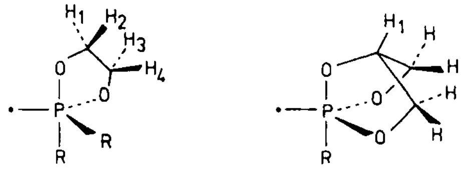


FIGURE 6 The experimental (upper trace) and computer simulated (lower trace) ESR spectrum of the tetrahedral radicals derived from compound **7**.



8 9

FIGURE 7 Model compounds **8** and **9** studied by Cooper *et al.*[11]

large number of phosphoranyl radicals incorporating a five-membered dioxaphospholane ring. They concluded that the ESR spectra of phosphoranyl radicals **8** (see Figure 7) exhibit a hyperfine splitting from only one of the quasi-apical ring protons H_1 or H_2.

Accompanying quantum chemical calculations showed that the quasi-apical *cis*-proton (H_1), which forms part of a *W*-plane arrangement with the orbital of the unpaired electron on phosphorus, is most likely to produce these splittings. Although their calculations predict coupling constants of 0.6–0.9 mT, hydrogen splittings of only 0.2–0.4 mT were actually found. This discrepancy is probably due to the occurrence of conformational changes in the dioxaphospholane ring, together with ligand exchange processes around phosphorus.[12] Their examination of radical compound **9** revealed a hyperfine splitting of 0.55 mT for H_1, which is in good agreement with the more rigid structure of this phosphorane.

In the present work, a hydrogen hyperfine splitting of 1.1 mT (1H) is found for the TBP-e type radical compound **6′** (see Figure 5). On the basis of the calculations and the experiments discussed above it can therefore be concluded that in the TBP-e radicals derived from compound **6** only one of the hydrogens of the *POCH*$_2$-group possesses the correct arrangement with the orbital of the unpaired electron on the phosphorus atom. Furthermore, the magnitude of the hydrogen splitting indicates that the flexibility of the benzoxaphosphole ring is indeed very small. It also indicates that, under the experimental conditions applied, pseudorotation processes are very unlikely to occur in this compound.[13]

Tetrahedral radicals. Due to the complexity of the spectra observed for the tetrahedral radical species generated from compounds **6** and **7**, in principle different assignments are possible. Some insight into the fine structure of the ESR-spectra has been achieved by careful examination of partly substituted analogues of compound **7**.

First of all, it is noteworthy that the exocyclic substituent attached to phosphorus is not responsible for any observable hyperfine splittings. This has been inferred from experiments in which, upon replacement of the —$N(CH_3)_2$ group by —C_6H_5 or —OCH_3, no changes in the hyperfine structure of the ESR-spectrum could be detected.

On the other hand it is also of interest to note that, in analogy to the features recorded for the TBP radicals, the hydrogens attached to the *POC*-carbon also play an active part in the completion of the spectral structure. This could be concluded from experiments performed with compounds in which the *POC*-hydrogens were replaced by methyl substituents. The *tentative* assignment of the remaining hyperfine splittings to the aromatic hydrogens is based on the examination of several partly substituted benzoxaphospholes. Ortho-, meta- and parasubstituted mono- and dimethoxybenzoxaphospholes were used to determine the magnitude of the hyperfine splittings of the *o*-, *m*- and *p*-H's. After computer simulation of the spectra obtained, the assignment could be made.[15]

It is concluded that the spectrum, consisting of 36 lines, contains the following hyperfine splittings: $a(\mathrm{P}) = 1.62\,\mathrm{mT}$, $a(p\text{-H}) = 1.56\,\mathrm{mT}$ (1H), $a(o\text{-H}) = 0.87\,\mathrm{mT}$ (1H), $a(m\text{-H}) = 0.16\,\mathrm{mT}$ (2H) and $a(\mathrm{CH_2}) = 0.54\,\mathrm{mT}$ (2H). These data are typical for a tetrahedral radical species and are in excellent agreement with those reported in previous work on analogous cyclic and acyclic tetrahedral phosphorus radicals[1a,3b,3d,6].

DISCUSSION

On the basis of the data presented above, it is now possible to determine the prerequisites necessary to observe the transformation of a TBP-e phenylphosphoranyl radical into the corresponding tetrahedral radical species. It can be concluded that the rigidity incorporated in the precursor TBP compounds is indeed the main reason for the stabilization of the corresponding TBP-e radical. Upon removal of some of the stabilizing factors, the actual transformation of a TBP into a tetrahedral radical species could be detected for the first time. Although the results do not provide a direct conclusive evidence for the hypothesis that, in general, all the reactions of P(III) compounds with addendum radicals proceed via a TBP phosphoranyl intermediate, it does show that in case phenylphosphoranyl radicals are involved, the isomerization will most likely take place by the pathway depicted in Figure 2.

CONCLUDING REMARKS

This study clearly demonstrates some important influences of the nature of the ligands around the central phosphorus atom on the ultimate radical structure. It is shown that a precursor phosphorane in which a rigid TBP backbone is incorporated gives rise to the formation of a TBP-e type radical species. If, on the other hand a tetrahedral precursor is used, only the tetrahedral radical is detected.

Upon reduction of the stability of the TBP backbone, e.g. by introducing a more flexible dioxaphospholane ring, the isomerization of the initially formed TBP-e radical into an energetically more stable tetrahedral radical species can be monitored. Moreover, this study further substantiates the hypothesis that, in general, reactions of P(III) compounds with other radical species proceed via TBP intermediate.

EXPERIMENTAL SECTION

Spectroscopy

All NMR spectra were run in the FT mode on a Bruker AC-200 spectrometer. The chemical shifts present in the ^{1}H and ^{13}C NMR spectra, which were recorded at 200.1 MHz and 50.3 MHz respectively, are referenced against TMS as internal standard ($\delta = 0$). The chemical shifts in the ^{31}P NMR spectra, recorded at 80.9 MHz, are related to 85% H_3PO_4 as external standard and are designated positive if downfield with respect to the reference. All spectra were recorded in $CDCl_3$ unless stated otherwise. The techniques employed for the detection of the ESR-spectra during continuous u.v. irradiation have been described previously.[1b] The electrochemical reduction of phosphonium salt **4** was performed in a flat ESR sample cell using platinum electrodes. The experiments were carried out using a DC current of 10 μA to 1 mA at a voltage of 0–400 V. The best results were obtained at 15 V and 0.3 mA. Spectral simulations were performed using the standard Gaussian simulation program.[16]

Synthesis

All solvents and commercial reagents were reagent grade and were dried prior to use with the appropriate drying agents. All moisture sensitive compounds were handled under a dry nitrogen atmosphere throughout the experiments.

2,2'-dibromobiphenyl. This compound was prepared from 1,2-dibromobenzene according to a literature procedure.[17] Mp: 80–81°C; Yield: 40%. ^{1}H NMR: δ 7.18–7.39 (m, 6H, ArH), 7.60–7.67 (m, 2H, *o*-H). ^{13}C NMR: δ 123.4 (C-Br), 127.0 (*o*-C), 129.3 (*p*-C), 130.9 (*m*-C), 132.5 (*m*-H), 142.9 (ipso-C).

Bis(2,2'-biphenylene)hydrogenphosphorane (**3**). The phosphorane was prepared from bis(2,2'-biphenylene)phosphoniumiodide according to a literature procedure.[18] Mp: 97°C; Yield: 57%. ^{1}H NMR (THF-d_8): δ 7.30–7.82 (m, 16H, ArH), 9.23 (d, 1H, P—H, $J_{P-H} = 453$ Hz). ^{31}P NMR (THF-d_8): δ −111.1.

Bis(2,2'-biphenylene)phosphoniumiodide (**4**). This compound was prepared from 2,2'-dibromobiphenyl according to a method described by Hellwinkel.[19] Mp: 297°C (dec.); Yield 73%. ^{1}H NMR (CD_3OD): δ 7.60–7.87 (m, 10H, ArH), 8.01–8.10 (m, 6H, ArH). ^{13}C NMR (CD_3OD): δ 118.0 (C-P$^+$), 125.2 (*o*-C), 132.2 (*m*-C), 132.6 (*m*-C), 138.7 (*p*-C), 147.6 (ipso-C). ^{31}P NMR (CD_3OD): δ 28.3.

9-Dimethylamino-9-phosphafluorene (**5**). This compound was prepared according to the method described by Allen *et al.*[20] Bp: 102°C (0.05 mm); Yield 37%. ^{1}H NMR: δ 2.45 (d, 6H, 2CH_3), 7.26–7.83 (m, 8H, ArH). ^{13}C NMR: δ 41.0 (2CH_3), 120.8 (*p*-C), 127.1 (*o*-C), 128.8 (*m*-C), 130.3 (*m*-C), 141.1 (P—C), 142.5 (ipso-C). ^{31}P NMR: δ 57.6.

4',4',5',5'-Tetramethyl-3H-2,1-benzoxaphosphole-1-spiro-2'-[1.3.2]-dioxaphospholan (**6**). This phosphorane was synthesized according to the method described by Dahl *et al.*[14] Mp: 98 – 100°C; Yield: 58%. ^{1}H NMR: δ 1.09 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 4.83–5.11 (m, 2H, $POCH_2$), 7.21–7.50 (m, 3H, ArH), 8.05 (t, 1H, *o*-H), 7.76 (d, 1H, P—H, $J_{P-H} = 732$ Hz). ^{31}P NMR: δ −32.5.

1-Dimethylamino-3H-2,1-benzoxaphosphole (**7**). The compound was obtained from the reaction of benzylalcohol and $(CH_3)_2NPCl_2$ according to a literature procedure.[14] Bp: 58°C (0.1 mm); Yield: 51%. ^{1}H NMR: δ 2.49 (d, 6H, 2CH_3), 5.03–5.43 (m, 2H, $POCH_2$), 7.23–7.50 (m, 4H, ArH). ^{31}P NMR: δ 136.5.

The substituted benzoxaphospholes used for the assignment of the hydrogen splittings in compound **7** were synthesized from the commerically available substituted benzylalcohols, except for the compound in which the *POC*-hydrogens were replaced by methyl substituents. This compound was prepared from 2-(2-bromophenyl)propan-2-ol according to the method described for **7**. The spectroscopic parameters of all compounds are essentially the same as those obtained for compound **7** and are therefore not reported separately.

ACKNOWLEDGEMENT

This investigation has been supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

REFERENCES

1. See e.g: (a) J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Perkin Trans. II*, 1211 (1981). (b) A. E. H. de Keijzer and H. M. Buck, *Phosphorus and Sulfur*, **31**, 203 (1987). (c) A. G. Davies,

M. J. Parrott and B. P. Roberts, *J. Chem. Soc., Perkin Trans. II,* 1066 (1976), and references cited therein.

2. E.g. vinyl- and imino(trialkoxy)phosphoranyl radicals, see W. G. Bentrude, *Acc. Chem. Res.*, **15,** 117 (1982), and references cited therein.
3. (a) W. G. Bentrude, M. Moriyama, H.-D. Mueller and A. E. Sopchik, *J. Am. Chem. Soc.*, **105,** 6051 (1983). (b) G. Boekestein, E. H. J. M. Jansen and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 118 (1974). (c) S. P. Mishra, M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 606 (1974). (d) A. G. Davies, M. J. Parrott and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 973 (1974).
4. M. C. R. Symons, *Mol. Phys.*, **30,** 1921 (1975).
5. B. P. Roberts and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. II,* 905 (1981).
6. J. H. H. Hamerlinck, P. Schipper and H. M. Buck, *J. Chem. Soc., Chem. Commun.* 975 (1980).
7. Attempts to synthesize additional model compounds in which the remaining oxygen atom in the benzoxa-moiety was replaced by a less electro-negative —N(R) group were not successful. The starting P(III) compound could be detected, but it was too unstable to allow a proper purification. Further experiments regarding the synthesis of compounds in which the five-membered ring in the benzoxaphosphole moiety was expanded to a six membered ring even failed to produce the precursor P(III) compounds.
8. Attempts to find evidence of additional free radicals, especially those involving TBP radicals, by investigating a large magnetic field range and using higher microwave power, were not successful.
9. (a) R. Rothuis, T. K. J. Luderer and H. M. Buck, *Recl. Trav. Chim. Pays-Bas,* **91,** 836 (1972). (b) R. Rothuis, J. J. H. M. Font Freide and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **92,** 1308 (1973).
10. Experiments performed with the corresponding phosphate compounds indeed showed that this type of radical is not produced by direct reaction of the peroxide radical with the benzoxa-moiety of the molecule. It is therefore justifiable to conclude that the second radical species is a secondary product resulting from the isomerization of the primary TBP-e radicals.
11. J. W. Cooper, M. J. Parrot and B. P. Roberts, *J. Chem. Soc., Perkin Trans. II,* 731 (1977).
12. R. W. Denis and B. P. Roberts, *J. Chem. Soc., Perkin Trans. II,* 140 (1975).
13. This is confirmed by a study by Dahl *et al.*,[14] in which the pseudorotation barrier of compound **6** has been determined to amount to 70.3 kJ. mol^{-1}. The magnitude of this barrier does not allow pseudorotation at the temperatures used in this study.
14. B. M. Dahl, O. Dahl and S. Trippett, *J. Chem. Soc., Perkin Trans. I,* 2239 (1981).
15. Unfortunately, it was not possible to confirm the assignment of the hyperfine splittings. An ENDOR study of the radical derived from compound **7** would probably give the necessary information for a more definite assignment. The match between the experimental and reconstructed spectrum, however, is so close that despite this minor uncertainty it may be concluded that the reconstructed and experimental spectra are essentially the same.
16. GS program, copyright Bruker Spectrospin AG, Switzerland.
17. H. Gilman and B. J. Gay, *J. Org. Chem.*, **22,** 447 (1957).
18. D, Hellwinkel, *Chem. Ber.*, **102,** 528 (1969).
19. D. Hellwinkel, *Chem. Ber.*, **98,** 576 (1965).
20. D. W. Allen and I. T. Millar, *J. Chem. Soc.* (*C*), 252 (1969).