© 1997 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 70, 397—403 (1997)

Spin Trapping of Phosphorus-Centered Radicals Produced by the Reactions of Dibenzoyl Peroxide with Organophosphorus Compounds

Yoshimi Sueishi* **and Yuzo Miyake**

Department of Chemistry, Faculty of Science, Okayama University, Tsushima Naka 3-1-1, Okayama 700

(Received July 8, 1996)

The reactions of dibenzoyl peroxide (BPO) with organophosphorus compounds have been studied by means of an ESR technique combined with spin trapping. The intermediate phosphorus-centered radicals were trapped by *N*-benzylidene-*t*-butylamine *N*-oxide (PBN) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). The spin adducts with a characteristic hyperfine coupling constant (hfcc) due to a phosphorus atom were observed. From identification of trapped radicals, possible mechanisms of the reactions have been proposed. The hfccs due to β-hydrogen and phosphorus atoms exhibited a large temperature dependence for phosphoranyl–PBN spin adducts, while for phosphinyl–PBN spin adduct the dependence was small. Based on the P and H hfccs, the conformational positions of the adducts trapped by PBN and DMPO are discussed.

Spin trapping is useful for elucidating the mechanisms of chemical reactions which are inferred from studies of the stable final products.[1] The trapping of short-lived free radicals as stable nitroxide radicals utilizes the scavenger properties of nitroso compounds. Recently, in the reactions of dibenzoyl peroxide (BPO) with diethylamine and diphenylamine, we used various kinds of traps for capturing transient radicals, the reaction mechanisms were discussed.[2]

It is recognized that a phosphorus(III) compound can react with a free radical to increase the coordination number to four and give a phosphoranyl radical.[3] In many reactions of organophosphorus compounds, intermediate free radicals having the radical center located on a phosphorus atom may be formed. At low temperature, Kochi and Krusic[4] have successfully detected the phosphoranyl radical formed by the addition of *t*-butoxy radicals to phosphines. However, since the phosphoranyl radical produced by addition of radical species undergoes subsequent α- and β-scissions,[5] it is difficult to detect the intermediate phosphoranyl radicals at room temperature by means of ESR.

In the present research, we have studied the spin-trapping reactions of phosphorus-centered radical with *N*-benzylidene-*t*-butylamine *N*-oxide (PBN) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), and the trapped radicals are identified. Taking into account the observed radicals, we proposed the primary process of the reaction between BPO and organophosphorus compound. The conformational assignments for crowed compounds can be made from the hyperfine coupling constants (hfccs) of ESR spectra. We examined the temperature dependences of the H and P hfccs for the PBN spin adducts, and the conformations of the spin adducts were established from the hfcc values.

Experimental

Materials. Triphenyl phosphite (TPPT), triethyl phosphite (TEPT), and diphenylphoshine (DPP) were purchased from Wako Pure Chemicals Co., Ltd., and used without further purification. Dibenzoyl peroxide (BPO), provided by Kishida Ltd., was purified from a chloroform–ethanol mixture. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was purchased from Tokyo Kasei Kogyo and recrystalized from a chloroform–ethanol mixture. The traps (PBN and DMPO) were obtained from Aldrich and used as received. Reagent-grade solvents were dried over Molecular Sieves 4A-1/16, and distilled before use.

ESR Measurements. A JEOL JES-FE3XG spectrometer equipped with a 100-kHz field modulator was used for the ESR measurements. Reactant solutions of BPO (about 2.5×10^{-2} mol dm^{-3}), phosphite (about 2.5×10^{-1} mol dm^{-3}), and the trap (about 1.3×10^{-1} mol dm^{-3}) were introduced separately into an H-shaped tube with a side tube for ESR measurements. After the solutions were degassed by freezing and thawing under vacuum, the solutions were mixed and transferred into the side tube. Spectral simulations were made with an attached computer. The *g*-values were estimated with the aid of a frequency counter (Advantest TR5214) and the *g*-value of DPPH.

Results and Discussion

Reactions of Triphenyl Phosphite (TPPT) and Triethyl Phosphite (TEPT) with Dibenzoyl Peroxide (BPO). BPO is allowed to decompose into benzoyloxyl radicals at high temperature (for instance 75 °C).[6] To examine the radical reaction of TPPT with BPO, the benzene solutions of BPO and TPPT were mixed at 75 °C. However, no ESR signal could be detected. When the trap PBN was added, there appeared three kinds of signals, as shown in Fig. 1. With time, two signals gradually diminish, and a new signal appears

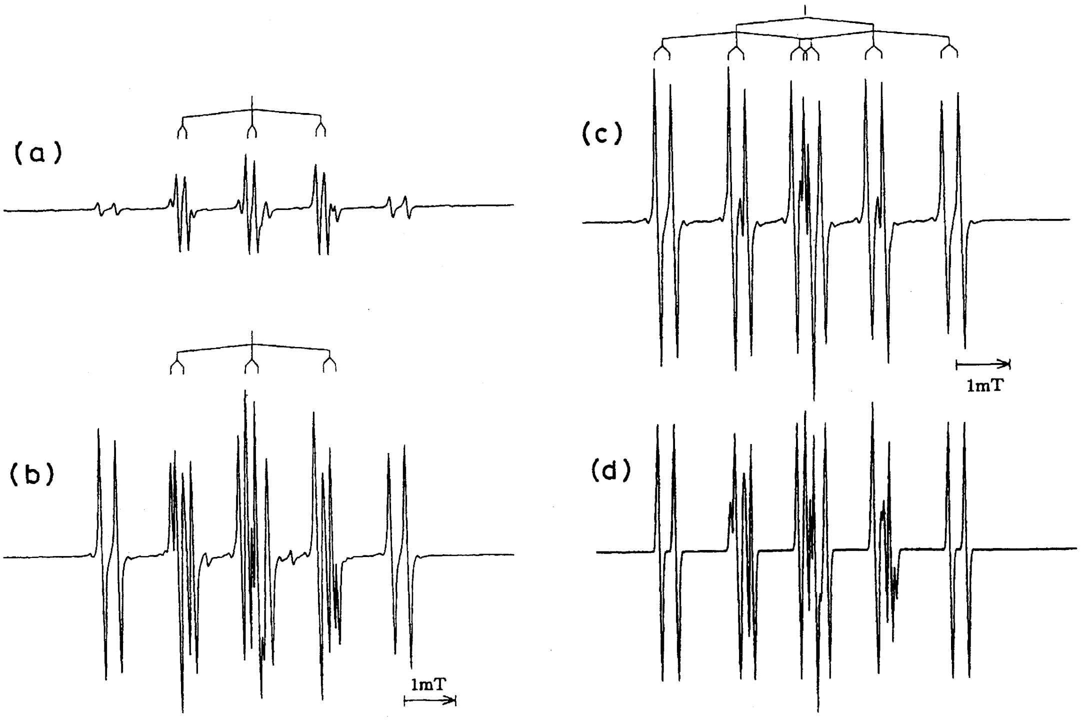
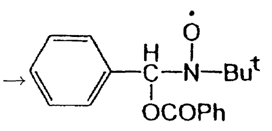


Fig. 1. ESR signals of the TPPT/BPO system in the presence of PBN in benzene at 75 °C. (a) Five minutes after mixing, (b) three hours after mixing, (c) twelve hours after mixing, and (d) simulation of b.

(Fig. 1c). The formed benzoyloxyl radical may decompose subsequently into phenyl radical and CO_2 at 75 °C.[6] Therefore, one of the observed ESR signals can be ascribed to benzoyloxyl–PBN spin adduct (**P-1**) with hyperfine coupling constants (hfcc) $a_N = 1.32$ mT and $a_H = 0.17$ mT. The other is due to phenyl–PBM spin adduct (**P-2**) with $a_N = 1.43$ mT and $a_H = 0.24$ mT. These hfcc values of **P-1** and **P-2** are in agreement with those observed previously for the reactions of BPO with amines.[2]

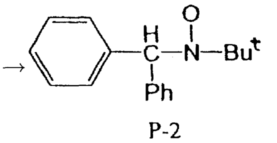
$$\mathrm{BPO} \rightarrow 2\mathrm{PhCOO}\cdot \qquad (1)$$

$$\mathrm{PhCOO}\cdot \rightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} \qquad (2)$$

PhCOO· + PBN →


(3)

P-1

Ph· + PBN →


(4)

P-2

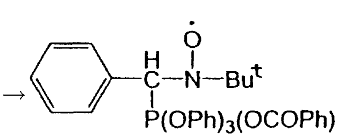
The remaining spin adduct **P-3** trapped by PBN shows characteristic doublet splitting. Judging from the g=value (2.0059), the adduct **P-3** is considered to be a kind of nitroxide radical. Each doublet with hfcc=2.64 mT splits into a triplet with hfcc=1.44 mT, and each triplet splits into a doublet with hfcc=0.31 mT. Though line broadening is not involved, a satisfactory fit of ESR spectrum at three hours after mixing was obtained by simulation using the ESR parameters of spin adducts **P-1**, **P-2**, and **P-3** (Fig. 1d). When much more PBN was added, the signals of **P-2** and **P-3** vanished and the signal of **P-1** alone was observed. This indicates that the radical PhCOO· is trapped exclusively by PBN, and deeply intervenes in the formation of the adduct **P-3**. Ramirez and McKelvie[3] suggested that phosphorus(III) compounds react with a free radical to increase the co-ordination number to four and give a phosphoranyl radical with nine valence electrons.

$$\mathrm{R}\cdot + \mathrm{PX_3} \rightarrow \mathrm{R\dot{P}X_3} \qquad (5)$$

Kochi and Krusic[4] detected a phosphoranyl radical when a solution of trimethylphosphine and di-*t*-butyl peroxide in cyclopropane was irradiated at low temperature. In the TPPT/BPO system, a similar reaction will take place:

$$\mathrm{BPO} \rightarrow 2\mathrm{PhCOO}\cdot \qquad (1)$$

$$\mathrm{P(OPh)_3} + \mathrm{PhCOO}\cdot \rightarrow \mathrm{(PhO)_3\dot{P}(OCOPh)} \qquad (6)$$

$\mathrm{(PhO)_3\dot{P}(OCOPh)}$ + PBN →


(7)

P-3

Addition of PhCOO· to the phosphorus atom of TPPT affords a phosphorus-centered radical, and the formed phosphoranyl radical may be trapped by PBN as a nitroxide radical. It is well known that the phosphorus-centered radicals exhibit unusually large doublet splitting (about 90 mT).[5] Therefore,

Table 1. ESR Parameters for the Observed Spin Adducts

Spin adduct	T		hfcc/mT		
	°C	g-value	a_P	a_N	a_H
P-1	75	2.0062		1.32	0.17
P-2	75	2.0061		1.43	0.24
P-3	75	2.0059	2.64	1.44	0.31
P-4	75	2.0058	2.52	1.43	0.31
P-5	25	2.0060	1.82	1.41	0.32
P-6	25	2.0057	1.71	1.41	0.38
D-3	75	2.0059	4.93	1.36	1.71
D-5	25	2.0057	3.72	1.36	1.83

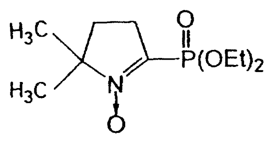

DEP-DMPO

Chart 1.

the ESR spectrum of **P-3** involving a phosphorus atom can be assigned to the spin adduct with a_P=2.64 mT, a_N=1.44 mT, and a_H=0.31 mT (Table 1). This spin adduct shows the characteristic large hfcc due to the phosphorus atom.

When DMPO was added to the TPPT/BPO system, the ESR signal with a characteristic doublet of hfcc=4.93 mT was observed. The ESR signal at three hours after mixing is shown in Fig. 2. Recently, Janzen and Zhang[7] synthesized a phosphorus-labeled DMPO (DEP–DMPO) (Chart 1): They showed that radical adducts of DEP–DMPO have the large phosphorus hfcc varying from 2.5 to 5.5 mT. Therefore, it is reasonable that the ESR spectrum in Fig. 2 be assigned to the phosphoranyl–DMPO adduct **D-3** with a_P=4.93 mT, a_N=1.36 mT, and a_H=1.71 mT. Using these ESR parameters, the observed ESR spectrum can be reproduced (Fig. 2b). The reaction scheme in this system is given below:

$$(PhO)_3P + PhCOO\cdot \rightarrow (PhO)_3\dot{P}(OCOPh) \qquad (8)$$

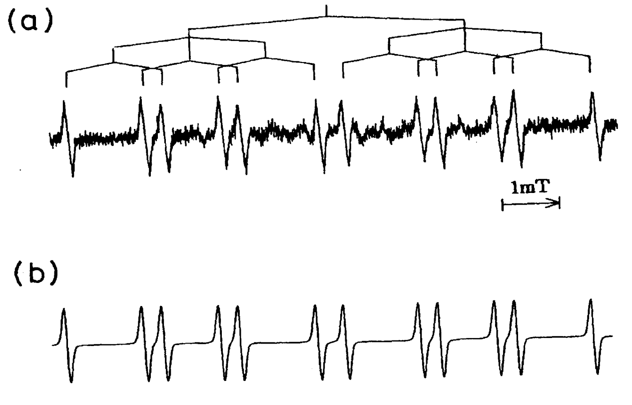


Fig. 2. ESR signals of the TPPT/BPO system in the presence of DMPO in benzene at 75 °C. (a) Three hours after mixing and (b) simulated spectrum.

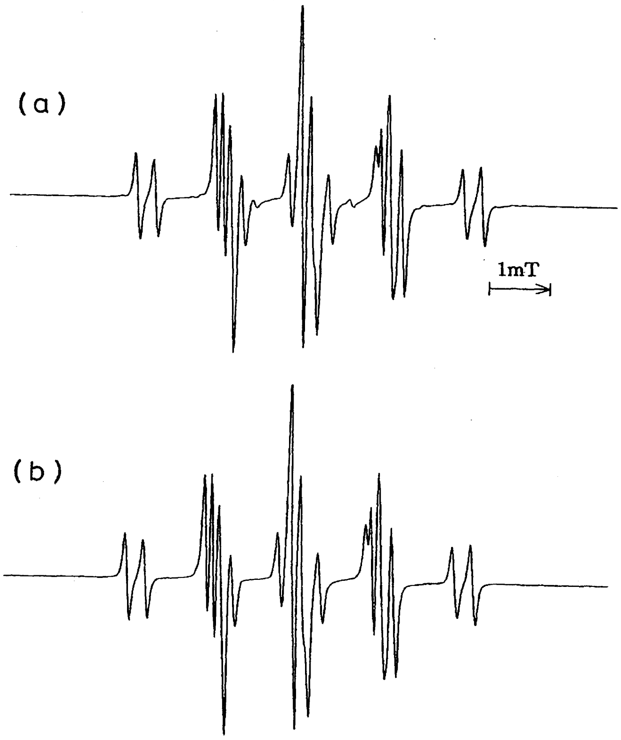
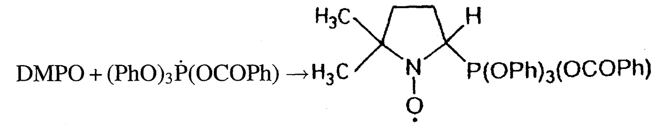


Fig. 3. ESR signals of the TEPT/BPO system in the presence of PBN in benzene at 75 °C. (a) Three hours after mixing and (b) simulated spectrum using ESR parameters of **P-1**, **P-2**, and **P-4**.



D-3

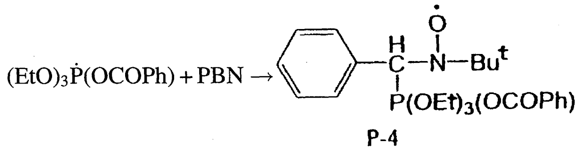
(9)

When TEPT was mixed with BPO in the presence of PBN at 75 °C, the ESR spectrum shown in Fig. 3 was obtained. The observed spectrum was reproduced well by means of the superposition of the simulation using the ESR parameters of three kinds of radicals (Fig. 3b), and thus reveals the presence of three adducts. In analogy with the case of the TPPT/BPO system, two of these can be assigned to benzoyloxyl–PBN adduct (**P-1**) and phenyl–PBN adduct (**P-2**). The remaining one has a characteristic hyperfine structure (hfs) with a large doublet hfcc. This radical is assignable to the phosphorus-centered radical adduct (**P-4**) trapped by PBN: a_P=2.52 mT, a_N=1.43 mT, and a_H=0.31 mT. As in the case of the TPPT/BPO system, the following reaction will take place:

$$BPO \rightarrow 2PhCOO\cdot \xrightarrow{PBN} \textbf{P-1} \qquad (10)$$

$$PhCOO\cdot \rightarrow Ph\cdot + CO_2 \xrightarrow{PBN} \textbf{P-2} \qquad (11)$$

$$PhCOO\cdot + (EtO)_3P \rightarrow (EtO)_3\dot{P}(OCOPh) \qquad (12)$$



P-4

(13)

When much more PBN was added, only the signal of **P-1** appeared, suggesting that the radical PhCOO· is necessary for the formation of **P-4**. The phosphoranyl radical would be produced by addition of PhCOO· to TEPT.

The Reaction of Diphenylphosphine (DPP) with BPO. Recently we studied the reactions of BPO with diphenylamine (DPA) by means of the ESR method combined with spin trapping, and suggested that the reaction proceeds via intermediate ion pairs at room temperature.[2] Since DPP has a structure similar to that of DPA, the reaction of BPO with DPP would take place at room temperature in analogy with the DPA/BPO system. In fact, when BPO (2.5×10^{-2} mol dm^{-3}) was mixed with DPP (2.5×10^{-1} mol dm^{-3}) in the presence of PBN (1.25×10^{-1} mol dm^{-3}), the ESR signals in Fig. 4 were obtained at room temperature. The signals comprise two components, which are regarded as nitroxide radicals from the *g*-values (Table 1). The signal patterns are similar to those of the phosphorus-centered radical adducts (**P-3** and **P-4**) observed for the TPPT and TEPT/BPO systems.

Taking into account the reaction mechanism of BPO with DPA, we now discuss the reaction mechanism of the DPP/BPO system. The following mechanisms involving an ion pair could be given, as suggested in the DPA/BPO system:

$$\mathrm{Ph_2PH + BPO \rightarrow \underset{IP_1}{[Ph_2\dot{P}^{+}H\ PhCOO^{-}]} + PhCOO\cdot} \qquad (14)$$

$$\mathrm{[Ph_2\dot{P}^{+}H\ PhCOO^{-}] \rightarrow \underset{\textbf{5}}{Ph_2P\cdot} + PhCOOH} \qquad (15)$$

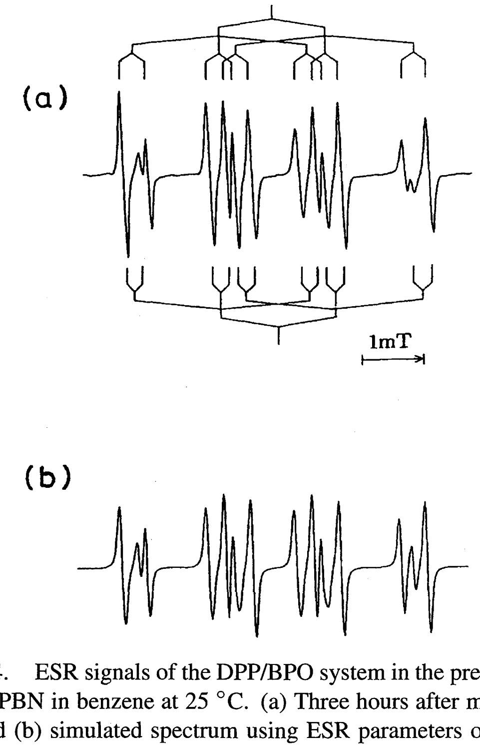
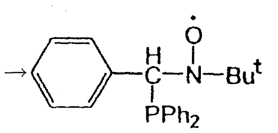


Fig. 4. ESR signals of the DPP/BPO system in the presence of PBN in benzene at 25 °C. (a) Three hours after mixing and (b) simulated spectrum using ESR parameters of **P-5** and **P-6**.

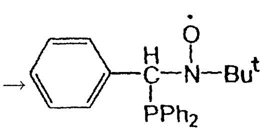
$$\mathrm{Ph_2PH + PhCOO\cdot \rightarrow \underset{\textbf{5}}{Ph_2P\cdot} + PhCOOH} \qquad (16)$$

Ph$_2$P· + PBN →

P-5 (17)

IP$_1$ denotes the ion pair within a solvent cage. By analogy with the case of amines,[2] the ion pair IP$_1$ formed between DPP and BPO may undergo rapid decomposition to give diphenylphosphinyl radical **5** and benzoic acid. The formation of benzoic acid was evidenced by product analysis. For the formation of the phosphinyl radical **5**, this process is independent of benzoyloxyl radical. On one hand, the formed benzoyloxyl radical may abstract the hydrogen atom of DPP to give the phosphinyl radical **5**. Accordingly, one of the spin adducts observed above can be assigned to the diphenylphosphinyl–PBN adduct **P-5** with $a_\mathrm{P}=1.82$ mT, $a_\mathrm{N}=1.41$ mT, and $a_\mathrm{H}=0.32$ mT.

To obtain further information on the diphenylphosphinyl radical **5**, DPPH was used instead of BPO. The stable free radical DPPH has been used not only as a radical scavenger but also as a hydrogen acceptor. The strong H-accepting property has been demonstrated by the hydrogen abstraction reactions of DPPH from the compounds containing C–H, N–H, O–H, and S–H.[8] DPPH exhibits a strong absorption around 520 nm. When DPP was mixed with DPPH, the absorption band in the vicinity of 520 nm decreased as time went by. We determined from the electronic spectrum that 2,2-diphenyl-1-picrylhydrazine (DPPH$_2$) was formed. DPPH abstracts the hydrogen atom of $\rangle$P–H and the diphenylphosphinyl radical **5** is produced. When the trap PBN was added to the DPP/DPPH system, there appeared one kind of ESR signal (Fig. 5). It is unequivocal that the observed signal corresponds to the diphenylphosphinyl–PBN adduct. This ESR spectrum agrees with that observed for the DPP/BPO system.

$$\mathrm{Ph_2PH + DPPH \rightarrow Ph_2P\cdot + DPPH_2} \qquad (18)$$

Ph$_2$P· + PBN →

(19)
P-5

The problem is how another spin adduct is formed from DPP. The reactions of BPO with amines involve ionic as well as radical processes via intermediate ion pairs.[2] Similarly, the ionic process of the reaction between DPP and BPO may occur to form benzoyloxydiphenylphosphine **7** through the following mechanism:

$$\mathrm{Ph_2PH + BPO \rightarrow \underset{IP_2}{[Ph_2\overset{+}{P}H\text{–}OCOPh\ \ PhCOO^{-}]}} \qquad (20)$$

$$\mathrm{[Ph_2\overset{+}{P}H\text{–}OCOPh\ \ PhCOO^{-}] \rightarrow \underset{\textbf{7}}{Ph_2P(OCOPh)} + PhCOOH} \qquad (21)$$

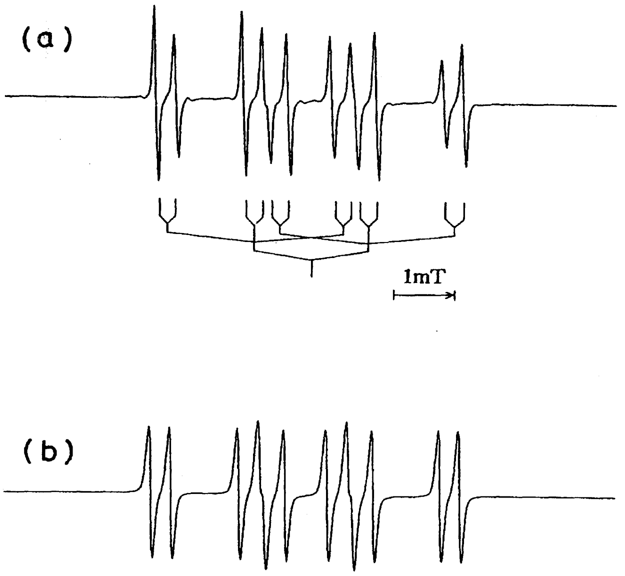
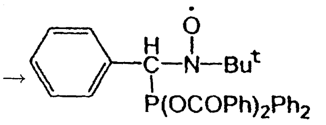


Fig. 5. ESR signals of the DPP/DPPH system in the presence of PBN in benzene at 25 °C. (a) Three hours after mixing and (b) simulated spectrum. [DPP]=2.5×10^{-1} mol dm^{-3}, [DPPH]=2.5×10^{-2} mol dm^{-3}, and [PBN]=1.3×10^{-1} mol dm^{-3}.

Phosphine **7** may react immediately with the radical PhCOO· to yield the phosphoranyl radical **6**:

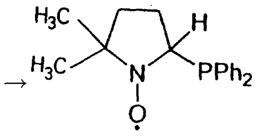
$$\mathrm{Ph_2P(OCOPh) + PhCOO\cdot \rightarrow \underset{\mathbf{6}}{Ph_2\dot{P}(OCOPh)_2}} \qquad (22)$$

$\mathrm{Ph_2\dot{P}(OCOPh) + PBN \rightarrow}$  (23)

P-6

The resulting phosphoranyl radical **6** will be trapped by PBN, and give the spin adduct **P-6**: a_P=1.71 mT, a_N=1.41 mT, and a_H=0.38 mT. Figure 4b represents the best fit spectrum calculated by the use of the ESR parameters of **P-5** and **P-6**. When much more PBN was added, the signal of **P-6** vanished and two kinds of the ESR signals of **P-1** and **P-5** were observed. The radical PhCOO· may be trapped exclusively before the formation of the radical **6**, suggesting that the radical PhCOO· intervenes in the formation of the radical **6**. Further, this indicates that the phosphinyl radical **5** is formed by decomposition of $\mathrm{IP_I}$ as well as by abstraction of a hydrogen atom from DPP.

When DMPO was used as spin-trap reagent, one kind of ESR signal (**D-5**) with the large doublet hfs was observed in the DPP/BPO system. Though the reason why the benzoyloxy radical can not be trapped by DMPO is not clear, the ESR spectrum was in agreement with that observed for the DPP/DPPH system in the presence of DMPO. Therefore, the characteristic hfs is assigned to the phosphorus atom of the dithenylphosphinyl–DMPO adduct **D-5**: a_P=3.72 mT, a_N=1.36 mT, and a_H=1.83 mT.

$\mathrm{Ph_2P\cdot + DMPO \rightarrow}$  (24)

D-5

Temperature Dependence of HFCC. There are many theoretical and experimental investigations which relate the hfccs of β-hydrogens to their conformational positions. It is instructive to discuss about the conformation of the spin adducts on the basis of H and P hfccs. For **P-3**, **P-5**, and **P-6** we have examined the temperature-dependence of β-H and P hfccs. The ESR signal pattern of these radicals was found to change with temperature. Representative ESR spectra for **P-3** are shown in Fig. 6. Since substantial line broadening that occurs from different types of molecular motions is not observed, the lineshape change may be ascribed to the change

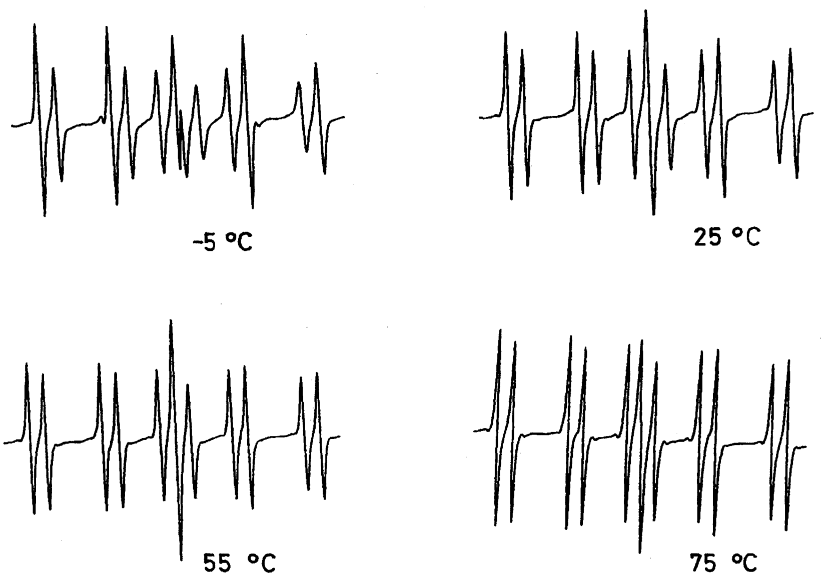


Fig. 6. Temperature dependences of ESR spectra of spin adduct **P-3**.

in the H and P hfccs. The H and P hfcc values, estimated from simulation of spectra at various temperatures, are given in Table 2. In Fig. 7, the H and P hfccs are plotted against temperature for **P-3** and **P-5**. The H hfcc of **P-3** and **P-6** decreases with temperature. On the other hand, the P hfcc increases with temperature. However, the H and P hfcc values for **P-5** are insensitive to temperature.

The dihedral angle between the p orbital of the nitroxide nitrogen and the C–H (C–P) bond is an important factor responsible for the value of hfcc, though other factors, such as the electronegativity and the bulkiness of the substituents, are operative. The angle dependences of the H and P hfccs are well established and can be expressed by:[9]

$$a_P\ (\mathrm{mT}) = 14.8\cos^2\delta \tag{25}$$

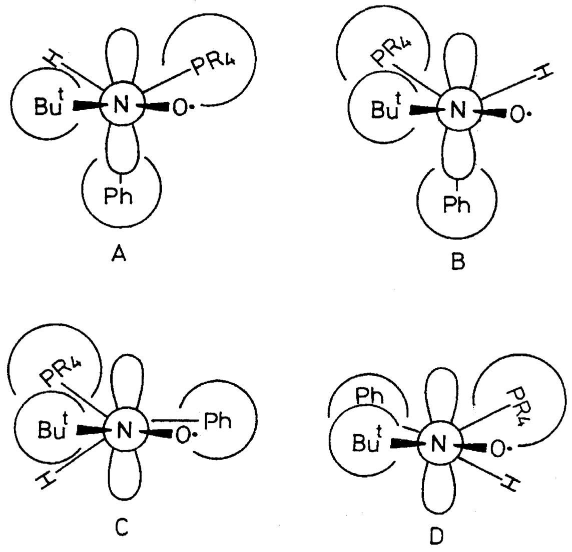
$$a_H\ (\mathrm{mT}) = 2.6\cos^2\theta \tag{26}$$

where δ and θ stand for the dihedral angles between the p orbital of the aminoxyl nitrogen atom and the C–P and C–H bonds, respectively. From the hfccs in Table 2, the δ and θ values of **P-3** can be estimated to be δ=66° (at −5 °C), 65° (at 75 °C) and θ=69° (at −5 °C), 70° (at 75 °C). It is found that the equilibrium position changes slightly with increasing temperature. The δ and θ values of **P-5** can be calculated to be 69°, independent of temperature. For the conformations around the C–N bond of **P-3**, the following four types are possible (Scheme 1): With the help of the Correy–Pauling–Koltum space-filling model (CPK), we have examined the equilibrium conformations of the spin adducts. In the conformations B and C (Scheme 1), the steric circumstance between Bu^t- and $\mathrm{PR_4}$-groups is very severe. In the conformation D, the steric hindrance between Ph and Bu^t-groups becomes severe. Therefore, our molecular model indicated that the equilibrium conformation of A is sterically feasible. For the temperature-dependence of hfccs, it can qualitatively be said that the steeper the torsional barrier becomes, the smaller the temperature coefficient is. However, the degree of crowdness around the C–N bond of **P-5** having three coodinates on the phosphorus atom is less severe than those of **P-3** and **P-6**. Though the temperature dependences of hfccs suggest the hindered internal rotation around the C–N bond for **P-3** and **P-6**, the rotation around that of **P-5**

Table 2. Variation of a_P and a_H with Temperature

T	**P-3** hfcc/mT[a]		**P-5** hfcc/mT[a]		**P-6** hfcc/mT[a]	
°C	a_P	a_H	a_P	a_H	a_P	a_H
−5	2.436	0.348	1.833	0.319	1.698	0.406
5	2.458	0.346	1.823	0.319	1.701	0.405
15	2.487	0.342	1.823	0.321	1.702	0.399
25	2.516	0.336	1.820	0.322	1.714	0.383
35	2.538	0.331	1.820	0.322	1.737	0.369
45	2.573	0.326	1.820	0.322	1.755	0.357
55	2.595	0.323	1.820	0.322	1.766	0.351
65	2.621	0.318	1.820	0.322	1.767	0.349
75	2.639	0.314	1.820	0.322	1.770	0.349

a) Precision within 1.5%.



Scheme 1.

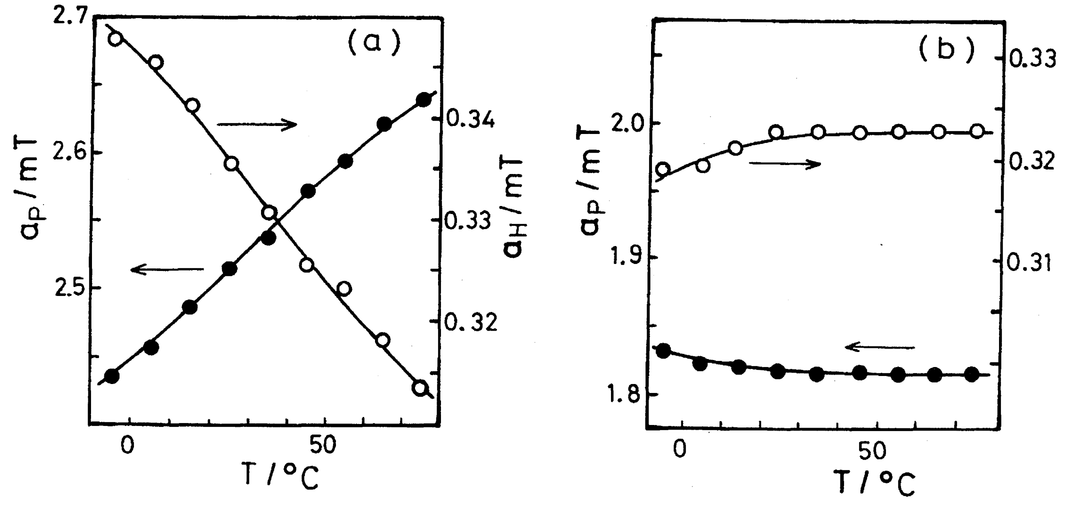


Fig. 7. Plots of hfccs against temperatures for (a) **P-3** and (b) **P-5**.

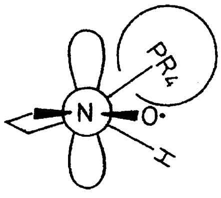


Chart 2.

seems not to be restricted, resulting in the insensitive nature of hfcc.

Owing to the 5-membered ring structure of DMPO, a possible type for the conformation around the C–N bond of **D-3** is depicted as follows (Chart 2): The δ and θ values of **D-3** can be estimated to be 55° and 36°, respectively. The difference in the δ values between **D-3** and **P-3** is small compared to that of the θ values. As predicted from the above equations, however, the a_P-value is about six times more sensitive to a variation in the dihedral angle than the a_H-value. Such findings show that phosphorus hfs is normally large and could be sensitive to the structure of spin adducts.

References

1) E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971).

2) N. Nishimura, T. Nakamura, Y. Sueishi, and S. Yamamoto, *Bull. Chem. Soc. Jpn.*, **67**, 1 (1994).

3) F. Ramirez and N. McKelvie, *J. Am. Chem. Soc.*, **79**, 5829 (1957); C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957).

4) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3944 (1969).

5) A. G. Davis, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 2224.

6) D. Swern, "Organic Peroxide," Willey-Interscience, New York (1970), Vol. 1.

7) E. G. Janzen and Y. -K. Zhang, *J. Org. Chem.*, **60**, 5441 (1995).

8) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, **1954**, 3574; J. C. McGowan and T. Powell, *J. Chem. Soc.*, **1961**, 2160; J. S. Hogg, D. H. Lohmann, and K. E. Russell, *Can. J. Chem.*, **39**, 1588 (1961); H. Watanabe and K. Kido, *Kogyo Kagaku Zasshi*, **60**, 1476 (1957).

9) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962); J. M. J. Tronchet, E. Winter-Mihaly, J. Rupp, and F. Barbalat-Rey, *Carbohydr. Res.*, **136**, 375 (1985).