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Synthesis of the *cis* diastereoisomer of 5-diethoxyphosphoryl-5-methyl-3-phenyl-1-pyrroline *N*-oxide (DEPMPPO*c*) and ESR study of its superoxide spin adduct

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Abstract—The *cis* and *trans* diastereoisomers of 5-diethoxyphosphoryl-5-methyl-3-phenyl-1-pyrroline *N*-oxide (DEPMPPO), the C(3)-phenyl analogue of DEPMPO, were prepared in three steps from phenylacetaldehyde and used in ESR-spin trapping of various carbon-, oxygen- and sulfur-centred radicals. In the case of the *cis*-isomer, the presence of the phenyl group cancels the alternating line width phenomenon observed for the DEPMPO–OOR (R = H, Bu^t) spin adducts. The ESR spectra of the DEPMPPO*c*–OOR spin adducts exhibit more straightforward patterns and are more easily assignable.

1. Introduction

The five-membered cyclic nitrones, DMPO **1** (5,5-dimethyl-1-pyrroline *N*-oxide) and DEPMPO **2** (5-diethoxyphosphoryl-5-methyl-1-pyrroline *N*-oxide) are widely used for the detection of free radicals by ESR-spin trapping experiments.[1] Largely as a result of the angular dependence of the β-proton splitting, these spin traps provide valuable information on the trapped radical. Moreover, the additional β-phosphorus coupling observed for DEPMPO adducts gives further reliability and confidence in the ESR assignments. The greater stability of the DEPMPO–OOH adduct compared to that of the analogue phosphorus-free DMPO–OOH adduct makes DEPMPO the reagent of choice for superoxide detection by ESR-spin trapping.[2] Moreover, peroxyl radicals are effectively trapped by DEPMPO in water and the distinction between peroxyl and alkoxyl spin adducts can be achieved unambiguously.[3]

The superoxide DEPMPO spin adduct exhibits a characteristic spectrum composed of a superimposition of two signals. The main signal results from addition of the superoxide radical on the less hindered face of DEPMPO (*trans* spin adduct, ▼, Figs. 2 and 3). The *cis* spin adduct, formed by addition on the other hindered face of DEPMPO, corresponds to the minor signal (♦, Figs. 2 and 3). The 12 expected lines of the main signal (*trans* spin adduct, ▼) exhibit an alternating line width effect and show the resolution of long range γ-hydrogen splittings from the pyrrolidine ring when low modulation amplitude is used (Fig. 3). This phenomenon is also observed for the alkylperoxyl adducts of DEPMPO. We have suggested that hindered rotation around the O–O peroxyl bond generates this alternating line width since this phenomenon was observed only in the case of the ROO$^{\bullet}$ (R = H, alkyl) spin adducts.[4] Rotation around the peroxyl bond induces conformational changes of the very flexible five-membered ring, thus resulting in the existence of two quickly exchanging conformers with significantly different values of the coupling constants. This alternating line width phenomenon was observed also with lower intensity for superoxide spin adduct of EMPO **3** (5-ethoxycarbonyl-5-ethyl-1-pyrroline *N*-oxide),[5] DEPPPO **4** (5-diethoxy-phosphoryl-5-phenyl-1-pyrroline *N*-oxide)[6] (Fig. 1) and DMPO **1**.[7]

To improve significantly the analysis of ESR spectra when the signal of either superoxide or alkylperoxyl is superimposed with the signal of other radicals, a number

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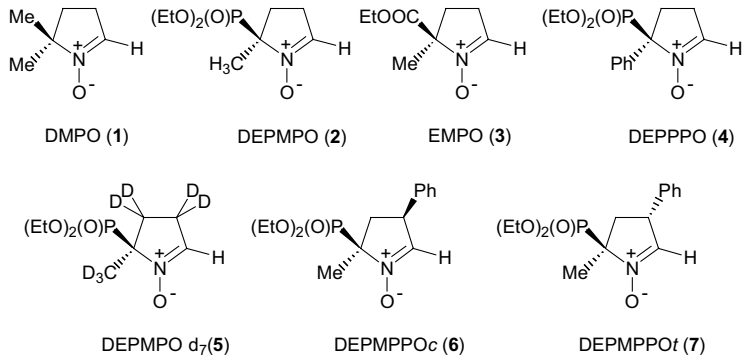


Figure 1. Chemical structures of DMPO and phosphorylated analogues.

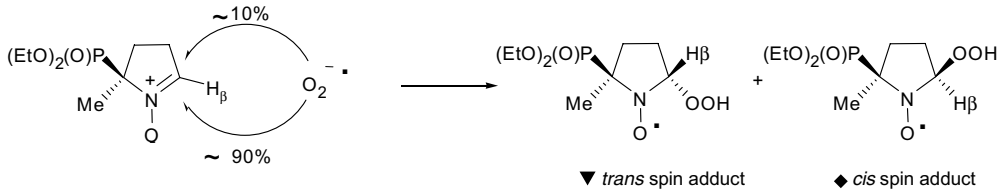


Figure 2. Trapping of superoxide with DEPMPO.

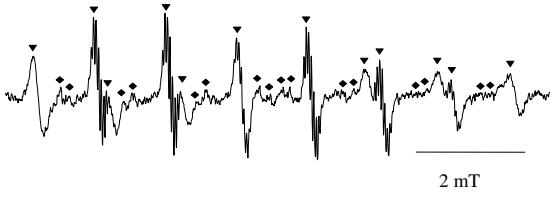
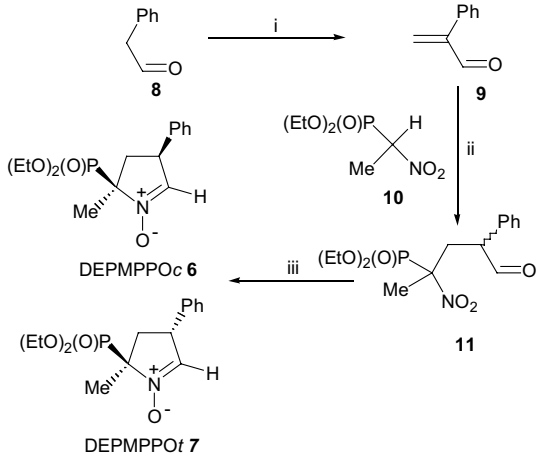


Figure 3. High resolution spectrum of DEPMPO–OOH in phosphate buffer.

of ^{2}H-labelled DEPMPO analogues were prepared (DEPMPO-d_7 **5**, Fig. 1). In this way, the complex spectra of DEPMPO–OOR (R = H, alkyl) adducts were simplified and their signal to noise ratio enhanced by the ^{2}H isotopic substitution of the γ-hydrogens of the pyrrolidine ring.[4] In earlier studies on stable β-phosphorylated five-membered ring nitroxides, the presence of a phenyl group on the pyrrolidine ring appeared to slow down the pseudorotation that occurs within the ring.[8] Moreover, Janzen and co-workers reported that the presence of a phenyl group in a DMPO spin trap analogue rigidifies the conformation of the corresponding spin adducts.[9] Therefore, to limit the internal motions in the spin adducts, we considered the 5-diethoxy-phosphoryl-5-methyl-3-phenyl-1-pyrroline *N*-oxide, a new C(3)-phenyl analogue of DEPMPO, as an attractive target. We report herein the synthesis of the two diastereoisomers, the *cis* and *trans* 5-diethoxyphosphoryl-3-phenyl isomers, and the ESR study of their use for the spin trapping of various radicals.

2. Synthesis

2-Phenylpropenal **9**[10] was prepared by reaction of phenylacetaldehyde **8** with tetramethyldiaminomethane in acetic anhydride.[11] 1,4-Addition of the nitrophosphonate **10**[12] on 2-phenyl propenal **9** in the presence of a catalytic amount of triethylamine in CH_3CN[13] afforded **11** as a mixture of two diastereoisomers in equal ratio, which was not resolved at this stage.[14] DEPMPPO was obtained through reductive cyclization by reaction of **11** with Zn and NH_4Cl (Scheme 1). The two DEPMPPO diastereoisomers were separated by column chromatography and further crystallization led to the pure DEPMPPO *cis* **6** and *trans* **7** diastereoisomers.[15] The stereochemistry of the *cis* isomer was determined by X-ray structure analysis (Fig. 4).



Scheme 1. Synthesis of the nitrones: (i) $Me_2NCH_2NMe_2$, Ac_2O, 1 h, 0 °C, 48%; (ii) Et_3N, CH_3CN, 2 h, 25 °C, 99%; (iii) Zn, NH_4Cl, THF/H_2O, 1 h, 0 °C, then 6 h at 25 °C, and chromatography: DEPMPPO*t* **7**, 27% and DEPMPPO*c* **6**, 25%.

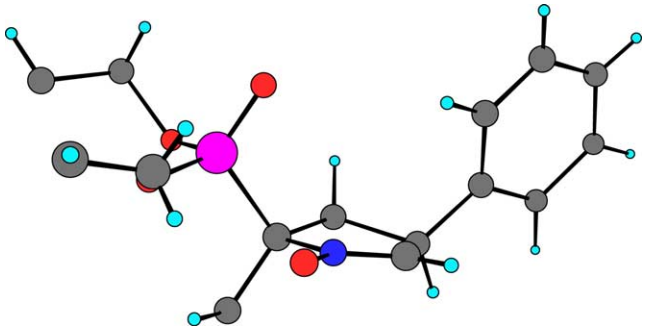


Figure 4. X-ray structure of the *cis* diastereoisomer **6** of DEPMPPO.

3. ESR studies[16]

3.1. Superoxide/Bu^{t}OO$^\cdot$

When DEPMPPO*c* **6** was reacted with superoxide, generated either from xanthin oxidase (XOD)/hypoxanthin (HX) or from KO_2, a spectrum consisting of 12 main lines was observed (Fig. 5a). This latter signal was completely suppressed in the presence of a high concentration of superoxide dismutase, while it was replaced by the DEPMPPO*c*–OH ESR signal in the presence of glutathion peroxidase and glutathione (GSH) (data not shown). Thus, the signal in Figure 5a can be attributed to the DEPMPPO*c*–OOH spin adduct. Similarly, an alkylperoxyl adduct of DEPMPPO*c* was obtained from the photolysis of Bu^{t}OOH in degassed toluene. These spectra are likely to correspond to a *trans* addition of the ROO$^\cdot$ (R = H, Bu^t) species on the face opposite to the *cis* related bulky phosphorus and phenyl groups. The dramatic alternating line width phenomenon, previously observed for DEPMPO–superoxide (Fig. 3) and -*tert*-butylperoxyl spin adducts, was not detected in the case of the DEPMPPO*c* adducts, the signals consist of 12 separated lines with almost the same intensity. Therefore, the following splittings for DEPMPPO*c*–OOH (a_N = 1.36, a_P = 3.35 and $a_{H\beta}$ = 1.81 mT) were derived from calculation without consideration of a chemical exchange for the computer simulation (Fig. 5b) (see Table 1). Unfortunately, the half-life time of the DEPMPPO*c*–OOH adduct was estimated to be only 2 min at pH 7.0, (data not shown) compared to the ~14 min half-life time observed for the DEPMPO–OOH under the same experimental conditions.[2]

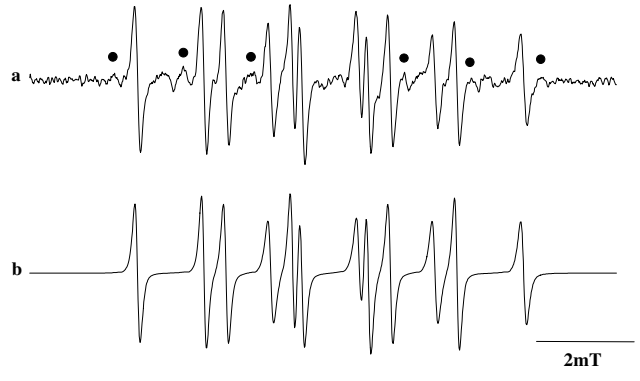


Figure 5. ESR signal of DEPMPPO*c*–superoxide adduct in water. (a) Signal obtained after 5 min incubation of DEPMPPO*c* (25 mM) with hypoxanthine (0.2 mM), xanthine oxidase (0.04 U/mL), DTPA (0.5 mM) in an oxygenated phosphate buffer (0.1 M, pH 7.4), (●) unidentified radical species; (b) computer simulation of the experimental spectrum (a).

Table 1. Simulated hyperfine coupling constants (mT) for DEPMPPO*c* **6** spin adducts[a]

Adduct	A_N	$A_{H\beta}$	A_P
6-OBu^t[b]	1.35	1.85	3.96
6-OOBu^t[b]	1.27	1.66	3.13
6-OH	1.43	2.02	3.87
6-OOH[c]	1.36	1.81	3.35
6-CO_2Na	1.46	2.45	3.67
6-$CH(CH_3)OH$	1.47	2.48	3.63
6-SG	1.37	2.11	2.94

[a] In phosphate buffer at pH 7 unless otherwise mentioned.
[b] In benzene.
[c] From XOD/HX system.

3.2. HO$^\cdot$ and other radicals

The hydroxyl radical adduct was obtained by reaction of DEPMPPO*c* **6** either by incubation with H_2O_2 and $FeSO_4$ or by UV photolysis of H_2O_2. The Fenton reaction was also carried out in the presence of HCO_2Na, EtOH or GSH to generate the corresponding $^\cdot CO_2^-$, $^\cdot CH(CH_3)OH$ and GS$^\cdot$ radical species. The ESR spectrum of the DEPMPPO*c*–OH adduct consists of 12 lines, compared to the doublet of quadruplet detected for the DEPMPO–OH adduct. Again in these reactions, it was assumed that the stereoselective addition occurred on the less hindered face of DEPMPPO*c*. The observed coupling constants are in the range 3.0–4.0 mT for phosphorus and 1.7–2.5 mT for β-hydrogen and they are characteristic of the added radicals (Table 1).

While the values of $a_{H\beta}$ and a_P for oxygen- (OH, OR, OOH and OOR), and sulfur-centred spin adducts of DEPMPO are in the range 0.8–1.2 and 4.8–5.2 mT, respectively, it is noteworthy that the corresponding DEPMPPO*c* adducts exhibit a greater hydrogen coupling and a rather small phosphorus splitting (Table 1). These differences traduce significant changes in the preferred geometries for the two series of spin adducts.

3.3. Structure–physical properties correlations

The ESR coupling constants of the DEPMPPO*c* spin adducts could be directly dependent on the pyrrolidine ring geometry and these geometric factors could influence the relative stabilities of the DEPMPO– and DEPMPPO*c*–superoxide adducts. In the case of DEPMPO–superoxide adducts, the low value of the hydrogen splitting ($\langle a_{H\beta}\rangle$ = 1.02 mT) indicates a pseudo-equatorial position of the H_β atom and a pseudo-axial position of the C–OOR (R = H, alkyl) group that favours the anomeric interaction between the π system of the nitroxyl group and the C–OOR bond.[17] Such a stabilization was observed by Janzen and co-workers in the case of the 6,6-dimethyl-1-piperidine *N*-oxide-superoxide spin

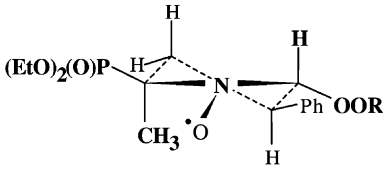


Figure 6. $^4T_3$ conformation of DEPMPPO*c*–peroxyl adduct.

adduct.[18] Moreover, the value of the phosphorus splitting ($a_P = 5.03$ mT) for DEPMPO–OOH indicates a pseudo-axial position of the P(O)(OEt)$_2$ group in both conformers (or mean conformers) undergoing the chemical exchange phenomenon. This position leads to a stabilizing hyperconjugative interaction of the C–P bond with the π system of the nitroxyl group. These two stabilizing interactions may explain in part the stability of DEPMPO–OOH. On the other hand, in the case of DEPMPPO*c*–OOH adduct the two bulky groups (diethoxyphosphoryl and phenyl) adopt both an equatorial position ($a_P = 3.35$ mT) to minimize the steric interactions. This gives rise to a unique preferred $^4T_3$ conformation in which the β-hydrogen adopts an axial position with a high splitting value ($a_{H\beta} = 1.81$ mT) (Fig. 6). In this case, the anomeric or hyperconjugative stabilizing interactions cannot take place and therefore, this nonstabilizing geometry could explain the rapid disappearance of the DEPMPPO*c*–OOH adduct.

When the radical additions were performed using the second diastereoisomer (DEPMPPO*t*, **7**) for which the two faces exhibit both similar steric hindrance, mixtures of diastereoisomeric spin adducts were observed, leading to complex ESR spectra. Therefore this *trans*-diastereoisomer **7** is less interesting for spin trapping experiments.

In conclusion, in the DEPMPPO*cis* isomer **6**, a new C(3)-phenyl analogue of DEPMPO, the phenyl group acts as an anchor probe, which blocks the pseudorotation of the pyrrolidine ring and which abolishes the alternating ESR line width phenomenon, observed with the DEPMPO superoxide and alkylperoxide adducts. Thus simpler spectra are obtained for the DEPMPPO*c* superoxide and peroxyl radical adducts. However, the conformational changes induced by the phenyl group lead to a considerable decrease of the lifetime of the superoxide spin adduct.

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10. *Synthesis of 2-phenylpropenal* **9**. Acetic anhydride (72.5 mL, 843 mmol) was added dropwise to a mixture of phenylacetaldehyde **8** (18.0 g, 150 mmol) and tetramethyldiaminomethane (63 mL, 456 mmol) at 0 °C. After stirring at room temperature for 1 h, ice-cold water (150 mL) was added and the mixture was extracted with Et_2O (6 × 50 mL). The organic phase was distilled under reduced pressure. The solution of the residue in CH_2Cl_2 (100 mL) was washed successively with an aqueous HCl solution (0.05 N, 40 mL), a saturated $NaHCO_3$ aqueous solution (30 mL) and brine (30 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give **9** (9.6 g, 48%) as a colourless liquid used directly in the next step. δ_H (200 MHz) 6.12 (1H), 6.65 (1H), 7.49–7.21 (5H, m), 9.80 (1H, s); δ_C (50.32 MHz) 127.89, 128.18, 128.56, 135.54, 135.63, 148.20, 192.94.
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14. *Synthesis of diethyl(2-nitro-5-oxo-4-phenyl-pentan-2-yl)-phosphonate* **11**. A solution of Et_3N (900 μL), 2-phenylpropenal **9** (9.6 g, 72 mmol) and diethyl 1-(1-nitroethyl)-phosphonate **10** (11.5 g, 54.6 mmol) in MeCN (50 mL) was stirred for 1.5 h and was then concentrated under reduced pressure to afford the nitrophosphonate **11** as a yellow oil (18.6 g, 97%); δ_P (40.53 MHz) 15.42, 15.17; δ_H (300 MHz) 1.30–1.42 (6H, m), 1.63 and 1.73 (3H, d, J_{H-P} 15.0 Hz), 2.35–2.77 (1H, m), 3.15–3.52 (2H, m), 3.77 (0.5H, t, *J* 6 Hz), 3.87 (0.5H, t, *J* 6 Hz), 4.19–4.26 (4H, m), 7.16–7.40 (5H, m), 9.55 and 9.61 (1H, s); δ_C (75.47 MHz) 16.06 and 16.13, 19.46 and 20.47, 34.10 and 34.5, 53.99 (d, J_{CP} 9.0 Hz) and 54.18 (d, J_{CP} 7.5 Hz), 64.19 (d, J_{CP} 7.5 Hz) and 64.36 (d, J_{CP} 6.8 Hz), 88.9 (d, J_{CP} 148.7 Hz) and 89.0 (d, J_{CP} 150.2 Hz), 128.1, 128.79 and 128.84, 129.13 and 129.23, 134.61 and 135.24, 196.98 and 197.28.

15. *Synthesis of 5-diethoxyphosphoryl-5-methyl-3-phenyl-1-pyrroline N-oxide (DEPMPPO)*: Zn dust (1.57 g, 24.0 mmol) was added by small portions over 1 h to a solution of the nitrophosphonate **11** (3.3 g, 9.62 mmol) and NH_4Cl (1.28 g, 24.0 mmol) in THF/H_2O (15/5 mL) at 0 °C. The mixture was stirred for 6 h at room temperature. After filtration and concentration under reduced pressure, water (10 mL) was added. The precipitate was filtered, washed with brine (10 mL) and the combined aqueous phases were extracted with CH_2Cl_2 (2 × 15 mL). The organic phase was dried over Na_2SO_4 and distilled under reduced pressure. The two diastereoisomers of DEPMPPO were isolated after column chromatography (silica gel, ethyl acetate/methanol 190/15) and crystallization in ether/pentane.
DEPMPPO*trans isomer* **7** (0.8 g, 27%); mp 85 °C; δ_P (40.53 MHz) 20.45; δ_H (300 MHz) 1.38 (6H, t, *J* 6.0 Hz), 1.75 (3H, d, J_{HP} 15.0 Hz), 1.90–2.0 (1H, m), 3.20–3.40 (1H, m), 4.15–4.45 (5H, m), 7.01 (1H, t, *J* 3.0 Hz), 7.15–7.40 (5H, m); δ_C (75.47 MHz) 16.4 (d, J_{CP} 5.3 Hz), 21.3, 42.0, 44.3, 62.8, 64.2 (d, J_{CP} 6.0 Hz), 75.6 (d, J_{CP} 153.5 Hz), 127.2, 127.6, 129.0, 137.2 (d, J_{CP} 7.5 Hz), 140.5 (d, J_{CP} 3.7 Hz); (found: C, 55.70; H, 7.22; N, 4.53; calcd for $C_{15}H_{22}NO_4P$: C, 57.87; H, 7.07; N 4.50%).
DEPMPPO*cis isomer* **6** (0.74 g, 25%); mp 65 °C; δ_P (40.53 MHz) 20.23; δ_H (300 MHz) 1.34 (3H, t, *J* 7.0 Hz), 1.37 (3H, t, *J* 7.0 Hz), 1.79 (3H, d, J_{HP} 16.0 Hz), 2.50–2.80 (2H, m), 4.10–4.45 (5H, m), 6.87–6.88 (1H, m), 7.20–7.45 (5H, m); δ_C (75.47 MHz) 16.3, 20.8, 40.1, 44.5 (d, J_{CP} 6.8 Hz), 62.6 (d, J_{CP} 6.8 Hz), 63.9 (d, J_{CP} 6.8 Hz), 76.1 (d, J_{CP} 163.8 Hz), 127.6, 127.9, 129.0, 136.1 (d, J_{CP} 8.3 Hz), 140.0; (found: C, 55.60; H, 7.19; N, 4.52; calcd for $C_{15}H_{22}NO_4P$: C, 57.87; H, 7.07; N 4.50%). Crystallographic data (excluding structure factors) for compound **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 235381.

16. *Hydroxyl radical*. Addition of an aqueous solution of $FeSO_4$ (1 mM) to the incubation mixture containing H_2O_2 (2 mM) and DEPMPPO*c* (25 mM) in phosphate buffer (0.1 M, pH 7.4) resulted in the observation of DEPMPPO*c*–OH adduct signal. *Carbon-centred radicals*. DMSO (10% v/v) was added to the Fenton system to generate the $CH_3^{\cdot}$ radical, EtOH (10% v/v) to get $CH_3\dot{C}H(OH)$ radical, HCOONa (200 mM) for $^{\cdot}COO$ and $NaHSO_3$ (50 mM) for $^{\cdot}SO_3$. *Superoxide anion radical*. The DEPMPPO*c*–superoxide adduct was obtained either by incubation of hypoxanthine (0.2 mM), xanthine oxidase (0.04 U/mL), DTPA (0.5 mM) and DEPMPPO*c* (50 mM) in an oxygenated phosphate buffer (07.1 M, pH 7.4) or by adding 5% v/v of an equimolar KO_2/18-crown-6 (0.1 M) DMSO solution to a deoxygenated phosphate buffer solution of DEPMPPO*c* (25 mM). $Bu^tOO^{\cdot}$. The DEPMPPO*c*–$OOBu^t$ adduct was obtained by UV-photolysis of a degassed solution of *t*-BuOOH (1.5 M) and DEPMPPO*c* (50 mM) in benzene. $Bu^tOO^{\cdot}$. DEPMPPO*c*–OBu^t was obtained by UV-photolysis of a degassed solution of Bu^tOOBu^t (0.5 M) and DEPMPPO*c* (50 mM) in toluene.

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