

## Inverted Spin Trapping. Part III.\* Further Studies on the Chemical and Photochemical Oxidation of Spin Traps in the Presence of Nucleophiles

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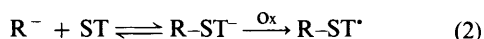
Inverted spin trapping, denoting the reaction between the radical cation of a spin trap ( $ST^{\bullet+}$ ) and a nucleophile ( $Nu^-$ ), has been further explored with respect to the photochemical generation of  $ST^{\bullet+}$  and the use of 5,5-dimethyl-1-pyrroline 1-oxide† (DMPO) and 3,3,5,5-tetramethyl-1-pyrroline 1-oxide‡ (TMPO) as ST. It is shown that photoexcitation of *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN) in the presence of a weak electron acceptor, tetrabutylammonium 12-tungstocobaltate(III), and a nucleophile gives the corresponding spin adducts,  $PBN-Nu^{\bullet}$ , most likely *via* the intermediate radical cation,  $PBN^{\bullet+}$ . This species could also be generated by sensitized photooxidation and made to react with  $Nu^-$ .

The cyclic *N*-oxides DMPO and TMPO are more difficult to oxidize than PBN (by 0.2–0.3 V). They both engage in inverted spin trapping, using both thermal and photochemical oxidation, but in a more restricted way than for PBN.

Ideally, spin trapping involves the reaction between an unknown radical  $R^{\bullet}$  and a spin trap (ST), a molecule containing a double bond which, upon addition of the radical, is converted into a persistent radical [eqn. (1)], the EPR characteristics of

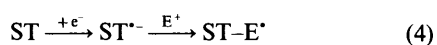
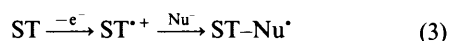


which can be studied at leisure and used for identification of the radical.<sup>1,2</sup> This scheme often works well, but alternative pathways to the spin adduct have been identified and warrant care in the interpretation of results of spin-trapping studies.<sup>1,3</sup> One problem is that spin traps usually are nitrones or nitroso compounds susceptible to addition of bases/nucleophiles,<sup>3</sup> in eqn. (2) symbolized by  $R^-$ , and the addition product, an oxy-



anion of a substituted hydroxylamine, is easily oxidized by even weak oxidants, such as dioxygen.

Another possibility for misinterpretation exists for attempted spin trapping reactions run under oxidizing/reducing conditions, the most prevalent case probably being photolysis. In this case one aims at showing that a nucleophile ( $Nu^-$ ) or electrophile ( $E^+$ ) undergoes one-electron oxidation or reduction by a redox reagent to give  $Nu^{\bullet}$  or  $E^{\bullet}$ , the detection of a spin adduct ( $Nu-ST^{\bullet}$  or  $E-ST^{\bullet}$ ) being taken as evidence for this redox step. However, as earlier<sup>1a,3</sup> and later repeatedly,<sup>4</sup> shown in isolated cases, the alternative mechanism, one-electron oxidation (reduction) of ST to give its radical cation (radical anion),  $ST^{\bullet+}$  ( $ST^{\bullet-}$ ), followed by its reaction with  $Nu^-$  ( $E^+$ ), will give the same spin adduct [eqns. (3) and (4)].



However, lack of systematic studies of these reaction types, in

combination with a previously rather limited background of electron transfer theory of organic molecules,<sup>5</sup> has delayed proper appraisal of these reactions for what they really are, namely a serious interpretational problem in many spin trapping studies.

It has recently been shown<sup>6</sup> that the use of a suitable oxidant, tris(4-bromophenyl)aminium ion ( $TBPA^{\bullet+}$ ), permitted studies of reaction (3) with a range of charged and uncharged nucleophiles. The fact that  $TBPA^{\bullet+}$  does not undergo electron transfer (ET) with certain nucleophiles<sup>7</sup> is an assurance that only ST becomes oxidized and thus reaction (3) must be the source of any spin adduct formed. In this particular case, ST was  $\alpha$ -phenyl-*N*-*tert*-butylnitron (PBN, IUPAC name *N*-benzylidene-*tert*-butylamine *N*-oxide), which is relatively easy to oxidize, its anodic peak potential being *ca.* 1.7 V *vs.* NHE (all potentials in the following will be given *vs.* NHE).<sup>4b</sup>  $E^{\circ}(TBPA^{\bullet+}/TBPA)$  is 1.30 V, which allows for a fast electron transfer step. A second reagent, hexachloroosmate ion [ $OsCl_6^-$  with  $E^{\circ}(Os^{VI}/Os^V) = 1.46$  V], could be used equally well<sup>8</sup> as the oxidant in eqn. (3) by virtue of the fact that its ET reaction with an anionic nucleophile is much slower than with a neutral molecule, given that their redox potentials are the same, due to the very strong electrostatic effects upon ET rates in a low relative permittivity solvent like dichloromethane. Even 4- $NO_2$ -PBN, with an anodic peak potential at *ca.* 2.2 V, underwent reaction (3) in some cases.<sup>8</sup>

The phenomenon that a spin adduct can be formed by capture of a polar species by a radical ion was denoted 'inverted spin trapping',<sup>6,8</sup> referring to the inverted distribution of electrons between the two reacting species as compared with ordinary spin trapping ( $ST^{\bullet+}/Nu^-$  *vs.*  $ST/Nu^{\bullet}$ ). Further illustrative cases of inverted spin trapping are now reported, emphasizing photochemical generation modes with PBN as the spin trap, and also explorative studies with other commonly used spin traps, such as 5,5-dimethyl-1-pyrroline 1-oxide (DMPO) and 3,3,5,5-tetramethyl-1-pyrroline 1-oxide (TMPO).

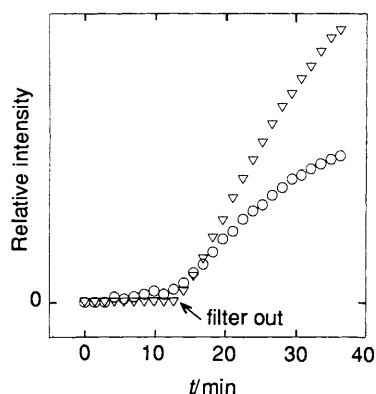
### Results

**Photochemical Generation of Spin Adducts from PBN.**—PBN has a UV spectral maximum at 296 nm ( $\log \epsilon = 4.0$ ) in dichloromethane. Photolysis with light of around this wave-

\* Part II, see Ref. 8.

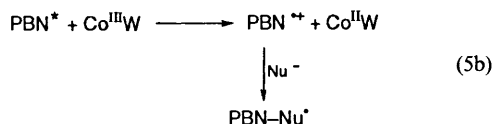
† IUPAC-recommended name: 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide.

‡ IUPAC-recommended name: 2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole 1-oxide.



**Fig. 1** Variation of the intensity of the EPR signal of  $(\text{Bu}')_2\text{NO}'$  upon photolysis of:  $\Delta$ , a solution of PBN ( $100 \text{ mmol dm}^{-3}$ ) in dichloromethane;  $\circ$ , a solution of PBN ( $100 \text{ mmol dm}^{-3}$ ) and  $\text{Co}^{\text{III}}\text{W}$  ( $2 \text{ mmol dm}^{-3}$ ) in dichloromethane. The initial period was run with filtered light (cut-off  $< 435 \text{ nm}$ ).

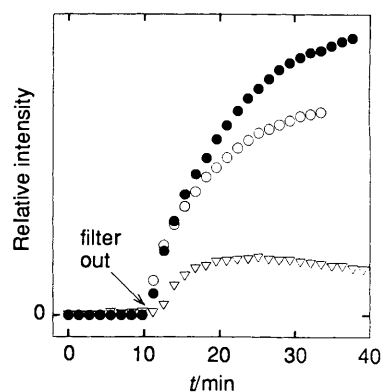
length in the presence of  $\text{Nu}^-$  and an otherwise inert electron acceptor should, at least partially [see eqn. (6) below], produce  $\text{PBN}^{\bullet+}$  which can either undergo back-ET or react with  $\text{Nu}^-$ . The tetrabutylammonium salt of 12-tungstocobaltate(III),  $(\text{Bu}_4\text{N})_5\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}$ , denoted for convenience  $\text{Co}^{\text{III}}\text{W}$ , was chosen as the acceptor, since it is a weak oxidant in dichloromethane [ $E^\circ(\text{Co}^{\text{III}}/\text{Co}^{\text{II}}) \sim 0.15 \text{ V}$ ]<sup>9</sup> and known to be a good model for an outer-sphere redox reagent.<sup>10</sup> Eqns. (5a) and (5b) show the reaction scheme for the generation of a spin adduct by this method.



In order to establish the fate of  $\text{PBN}^{\bullet+}$  in the *absence* of a nucleophile, a solution of PBN ( $100 \text{ mmol dm}^{-3}$ ) and  $\text{Co}^{\text{III}}\text{W}$  ( $2 \text{ mmol dm}^{-3}$ ) in dichloromethane was irradiated with filtered light (cut-off  $< 435 \text{ nm}$ ) from a 50 W high-pressure Hg lamp (Bruker ER 202 UV-irradiation system) in the EPR cavity. Two EPR signals appeared, one a very weak and eventually disappearing triplet with  $a^{\text{N}} = 0.80 \text{ mT}$  originating from the carbonylaminoxyl radical [ $\text{PhCON}(\text{O}')\text{Bu}'$ , lit.,<sup>2</sup>  $a^{\text{N}} = 0.80 \text{ mT}$ , denoted PBNOx in the following] and a stronger one (triplet,  $a^{\text{N}} = 1.58 \text{ mT}$ ) originating from the di(*tert*-butyl)aminoxyl radical [ $(\text{Bu}')_2\text{NO}'$ , lit.,<sup>2</sup>  $a^{\text{N}} = 1.584 \text{ mT}$ ]. The intensity of the di(*tert*-butyl)aminoxyl signal increased slowly with irradiation time [Fig. 1 ( $\circ$ )]. Removal of the filter strongly increased the rate of production of di(*tert*-butyl)aminoxyl radical. A reference experiment with PBN alone in dichloromethane showed similar features: no di(*tert*-butyl)aminoxyl radical production with filtered light and a strong increase in radical concentration with unfiltered light, in fact stronger than with  $\text{Co}^{\text{III}}\text{W}$  present [Fig. 1 ( $\Delta$ )].

Similar photolysis of PBN/ $\text{Co}^{\text{III}}\text{W}$  in acetonitrile, with water ( $0.50 \text{ mol dm}^{-1}$ ) present, gave the same EPR signals, but this time with that of PBNOx much larger than the  $1.58 \text{ mT}$  triplet from the di(*tert*-butyl)aminoxyl radical.

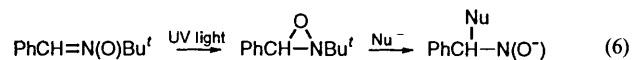
Irradiation of a solution of PBN ( $90 \text{ mmol dm}^{-3}$ ), triethyl phosphite ( $100 \text{ mmol dm}^{-3}$ ) and  $\text{Co}^{\text{III}}\text{W}$  ( $2 \text{ mmol dm}^{-3}$ ) with filtered light (cut-off  $< 435 \text{ nm}$ ) in the EPR cavity produced a



**Fig. 2** Variation of the intensity of the EPR signal of  $\text{PBN}-\text{P}(\text{OEt})_3^+$  upon photolysis of:  $\circ$ , a solution of PBN ( $90 \text{ mmol dm}^{-3}$ ) and triethyl phosphite ( $100 \text{ mmol dm}^{-3}$ ) in dichloromethane;  $\bullet$ , a solution of PBN ( $90 \text{ mmol dm}^{-3}$ ), triethyl phosphite ( $100 \text{ mmol dm}^{-3}$ ) and  $\text{Co}^{\text{III}}\text{W}$  ( $2 \text{ mmol dm}^{-3}$ ) in dichloromethane.  $\Delta$  represents the unidentified  $3 \times 2$  signal in experiment ( $\bullet$ ). The initial period was run with filtered light (cut-off  $< 435 \text{ nm}$ ).

weak signal of a spin adduct of unknown origin ( $3 \times 2$ ,  $a^{\text{N}} = 1.45 \text{ mT}$ ,  $a^{\text{H}} = 0.23 \text{ mT}$ ) but none of the triethoxyphosphonio adduct. Removal of the filter caused the EPR signal of latter adduct ( $a^{\text{P}} = 2.34 \text{ mT}$ ,  $a^{\text{N}} = 1.47 \text{ mT}$ ,  $a^{\text{H}} = 0.342 \text{ mT}$ ; lit.,<sup>6</sup>  $a^{\text{P}} = 2.33 \text{ mT}$ ,  $a^{\text{N}} = 1.47 \text{ mT}$ ,  $a^{\text{H}} = 0.345 \text{ mT}$ ) to appear immediately [see Fig. 2 ( $\bullet$ )] and grow rapidly with irradiation time. Also, the  $3 \times 2$  signal increased in intensity to a plateau value (Fig. 2 ( $\Delta$ )). A reference experiment without  $\text{Co}^{\text{III}}\text{W}$  revealed that  $(\text{EtO})_3\text{P}^+$  spin adduct builds up rapidly, although not as fast as with  $\text{Co}^{\text{III}}\text{W}$  present.

It is known<sup>11</sup> that photolysis of PBN with UV light leads to the cyclized, fairly stable product, 2-*tert*-butyl-3-phenyloxaziridine, which, at least in theory, might lead to an oxy-anion of a hydroxylamine by reaction with a nucleophile [eqn. (6)]; as already pointed out [eqn. (2)], the oxy-anion should



then be easily oxidized to the spin adduct. To test this possibility, a solution of PBN in dichloromethane was irradiated with unfiltered light for 15 min in order to build up the concentration of 2-*tert*-butyl-3-phenyloxaziridine. The resulting solution showed only the EPR signal of di(*tert*-butyl)aminoxyl radical, as expected. Addition of triethyl phosphite under argon in the dark did not produce any  $(\text{EtO})_3\text{P}^+$  spin adduct during a period of 30 min, nor did bubbling with dioxygen for 2 min in the dark, followed by argon degassing. In both cases, irradiation with unfiltered light immediately caused the EPR signal of the  $(\text{EtO})_3\text{P}^+$  spin adduct to appear in the same way as in Fig. 2.

Acetate ion is of unique diagnostic value for establishing inverted spin trapping, since the very high rate of decarboxylation of acetoxy radical (*ca.*  $10^9 \text{ s}^{-1}$ )<sup>12</sup> precludes its trapping by PBN. Photolysis of a solution of PBN ( $180 \text{ mmol dm}^{-3}$ ),  $\text{Bu}_4\text{N}(\text{AcO})_2\text{H}$  ( $65 \text{ mmol dm}^{-3}$ ) and  $\text{Co}^{\text{III}}\text{W}$  ( $2 \text{ mmol dm}^{-3}$ ) with filtered light (cut-off  $< 435 \text{ nm}$ ) gave two weak EPR signals, one nitrogen triplet with  $a^{\text{N}} = 1.57 \text{ mT}$  due to the di(*tert*-butyl)aminoxyl radical and one with a  $3 \times 2$  pattern ( $a^{\text{N}} = 1.35 \text{ mT}$ ,  $a^{\text{H}} = 0.156 \text{ mT}$ ), the latter corresponding to the acetoxy spin adduct (lit.,<sup>2,6</sup>  $a^{\text{N}} = 1.34\text{--}1.37$ ;  $a^{\text{H}} = 0.14\text{--}0.17$ ). Removal of the filter caused the triplet to grow rapidly, but did not notably affect the  $\text{PBN}-\text{OAc}^{\bullet}$  signal (Fig. 3).

Initial attempts to detect the fluorine adduct of PBN by photolysis of solutions of PBN ( $100 \text{ mmol dm}^{-3}$ ),  $\text{Bu}_4\text{NF}$ ,

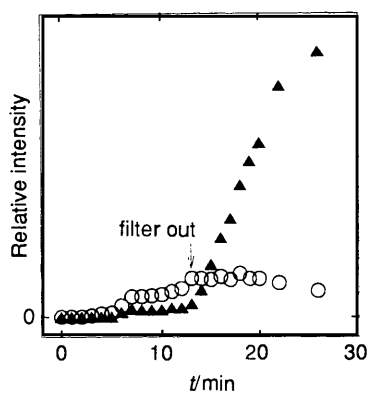


Fig. 3 Variation of the intensity of the EPR signal of PBN-OAc' (O) and (Bu')<sub>2</sub>NO' (Δ) upon photolysis of a solution of tetrabutylammonium hydrogen-diacetate (65 mmol dm<sup>-3</sup>), PBN (180 mmol dm<sup>-3</sup>) and Co<sup>III</sup>W (2 mmol dm<sup>-3</sup>) in dichloromethane. The initial period was run with filtered light (cut-off < 435 nm).

3H<sub>2</sub>O (140 mmol dm<sup>-3</sup>) and Co<sup>III</sup>W (4 mmol dm<sup>-3</sup>) with unfiltered light in dichloromethane were unsuccessful, and only the signal of the di(*tert*-butyl)aminoxyl radical was detected. This failure was eventually traced to the presence of small amounts of tributylamine in the fluoride salt<sup>8</sup> which could be removed by pumping on the salt at 0.1 mmHg overnight. Tributylamine is easily oxidized and thus reacts preferentially with PBN<sup>+</sup>. With the purified salt, the EPR signal of the fluorine adduct ( $a^F = 4.51$  mT,  $a^N = 1.27$  mT,  $a^H = 0.117$  mT, lit.,<sup>6</sup>  $a^F = 4.57$ ,  $a^N = 1.27$ ,  $a^H = 0.105$  mT) appeared, still with a strong signal of the di(*tert*-butyl)aminoxyl radical present. There was no sign of the EPR spectrum of difluorinated PBN, PhCF<sub>2</sub>N(O')Bu', found when tris(4-bromophenyl)ammonium ion was used as the oxidant.<sup>6</sup>

Since fluoride ion is a relatively strong base, the mechanism shown in eqn. (2) might be feasible. However, no signal from PBN-F<sup>•</sup> was observed in dichloromethane without irradiation with UV light, in spite of the fact that Co<sup>III</sup>W should be capable of oxidizing PhCH(F)N(O')Bu'. A check with dioxygen (bubbling the PBN-Bu<sub>4</sub>NF solution in dichloromethane with dioxygen for 30 s, followed by 15 min standing in the dark and final degassing with argon) as the oxidant instead of Co<sup>III</sup>W, gave no EPR signal whatsoever.

The equilibrium of eqn. (2) should be dependent on the solvation properties and relative permittivity of the solvent, and therefore a PBN-Bu<sub>4</sub>NF solution in CDCl<sub>3</sub> (relative permittivity = 4.7) was oxidized by dioxygen, using the same procedure as above. A medium intensity signal of PBN-F<sup>•</sup> was obtained ( $a^F = 4.45$  mT,  $a^N = 1.28$  mT,  $a^H = 0.129$  mT), together with a triplet of similar intensity due to the di(*tert*-butyl)aminoxyl radical. With Co<sup>III</sup>W as the oxidant, the same signal from PBN-F<sup>•</sup> was observed. In benzene, a similar experiment gave no signal, in all probability because of the very low solubility of the fluoride salt in benzene.

Fig. 4 shows the EPR spectral behaviour of a dichloromethane solution of PBN (160 mmol dm<sup>-3</sup>), Bu<sub>4</sub>NCl, H<sub>2</sub>O (150 mmol dm<sup>-3</sup>) and Co<sup>III</sup>W (2 mmol dm<sup>-3</sup>) upon irradiation with light, first filtered (cut-off < 435 nm) and then unfiltered. The characteristic signal of PBN-Cl' ( $a^N = 1.27$  mT,  $a^H = 0.082$  mT,  $a^{Cl-35} = 0.605$  mT,  $a^{Cl-37} = 0.47$  mT; lit.,<sup>2</sup> in acetonitrile  $a^N = 1.27$  mT,  $a^H = 0.082$  mT,  $a^{Cl-35} = 0.62$  mT,  $a^{Cl-37} = 0.512$  mT) appeared with the onset of the unfiltered light and its concentration increased to a steady state value; when irradiation was stopped, the signal rapidly decayed (half-life ~ 1 min).

Attempts to monitor the cyano spin adduct by irradiation of a solution of PBN, tetrabutylammonium cyanide and Co<sup>III</sup>W in dichloromethane failed owing to the interference of two

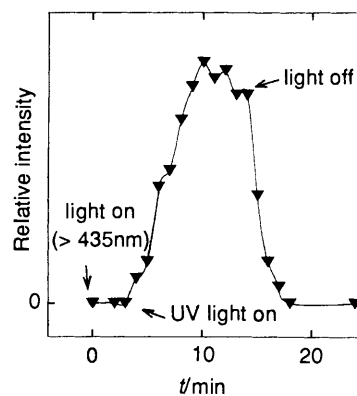


Fig. 4 Variation of the intensity of the EPR signal of PBN-Cl' upon photolysis of a solution of Bu<sub>4</sub>NCl:H<sub>2</sub>O (150 mmol dm<sup>-3</sup>), PBN (160 mmol dm<sup>-3</sup>) and Co<sup>III</sup>W (2 mmol dm<sup>-3</sup>) in dichloromethane. The initial period was run with filtered light (cut-off < 435 nm). The points have been joined by lines only in order to improve readability.

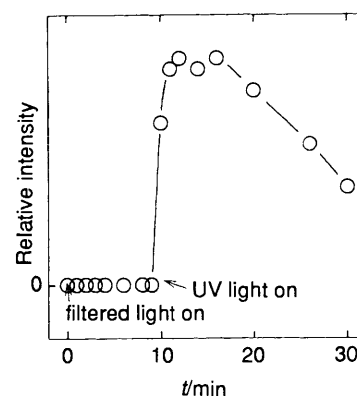


Fig. 5 Variation of the intensity of the EPR signal of PBN-CN' upon photolysis of a solution of Bu<sub>4</sub>NCN (100 mmol dm<sup>-3</sup>), PBN (100 mmol dm<sup>-3</sup>) and Co<sup>III</sup>W (2 mmol dm<sup>-3</sup>) in CDCl<sub>3</sub>. The initial period was run with filtered light (cut-off < 435 nm). The points have been joined by lines only in order to improve readability.

other signals, one being the ubiquitous (Bu')<sub>2</sub>NO' triplet and the other a triplet of doublets of unknown origin ( $a^N = 1.47$  mT,  $a^H = 0.30$ ). However, in CDCl<sub>3</sub> the signal from PBN-CN' appeared as soon as the > 435 nm filter was removed (see Fig. 5;  $a^N = 1.46$  mT,  $a^H = 0.23$  mT; lit.,<sup>6</sup> in dichloromethane,  $a^N = 1.51$  mT,  $a^H = 0.20$  mT). No cyano spin adduct appeared after oxidation of a solution of PBN and tetrabutylammonium cyanide with dioxygen.

When tetrabutylammonium tetramethylsuccinimide (denoted Bu<sub>4</sub>NT, 40 mmol dm<sup>-3</sup>) was photolysed with unfiltered light together with PBN (160 mmol dm<sup>-3</sup>) and Co<sup>III</sup>W (2 mol dm<sup>-3</sup>) in dichloromethane, the EPR spectrum of PBN-T<sup>•</sup> appeared immediately ( $a^N = 1.43$  mT,  $a^H = 0.51$ ,  $a^{N'} = 0.122$ ; lit.,<sup>6</sup>  $a^N = 1.43$  mT,  $a^H = 0.52$ ,  $a^{N'} = 0.133$ ), together with the (Bu')<sub>2</sub>NO' triplet. Since T<sup>-</sup> is a base of medium strength (pK of TH is 10–11), a check was made for the possible intervention of the PBN-T<sup>-</sup> adduct; oxidation by dioxygen or Co<sup>III</sup>W in dichloromethane did not give any PBN-T<sup>•</sup> whereas in CDCl<sub>3</sub> a medium-intensity signal ( $a^N = 1.44$  mT,  $a^H = 0.55$ ,  $a^{N'} = 0.116$ ) was obtained after oxidation by dioxygen.

Finally, in view of the general interest in the hydroxyl adduct of PBN,<sup>2</sup> some experiments aimed at generating this spin adduct by the method of eqn. (5) were performed. This adduct is unstable with a decay rate constant of ca. 0.07 s<sup>-1</sup> in acetonitrile.<sup>13</sup> It is produced by UV irradiation of a solution of PBN in a suitable solvent in the presence of 1% hydrogen peroxide,<sup>13</sup> a situation which is analogous to that shown in eqn. (5), with H<sub>2</sub>O<sub>2</sub> as the electron acceptor instead of Co<sup>III</sup>W

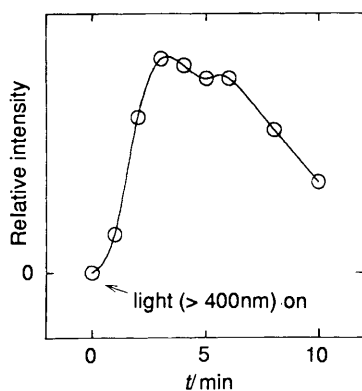


Fig. 6 Variation of the intensity of the EPR signal of PBN-T upon photolysis of a solution of tetrabutylammonium tetramethylsuccinimidate ( $\text{Bu}_4\text{NT}$ ,  $80 \text{ mmol dm}^{-3}$ ), PBN ( $100 \text{ mmol dm}^{-3}$ ) and 2,4,6-tri(methoxyphenyl)pyrylium tetrafluoroborate ( $7 \text{ mmol dm}^{-3}$ ) in dichloromethane. Filtered light (cut-off  $< 435 \text{ nm}$ ) was used. The points have been joined by lines only in order to improve readability.

and water, present from the use of 30%  $\text{H}_2\text{O}_2$  as the source of hydrogen peroxide, as the nucleophile. In our hands, this system gave two EPR signals after 30 s irradiation with unfiltered light, namely the triplet of  $(\text{Bu}')_2\text{NO}^\bullet$  and the  $3 \times 2$  pattern of PBN-OH $^\bullet$  ( $a^N$  1.476 mT,  $a^H = 0.267 \text{ mT}$ ; lit.,<sup>13</sup>  $a^N$  1.474 mT,  $a^H = 0.275 \text{ mT}$ ). Continued irradiation for another 150 s increased the former signal and decreased the latter one.

The use of  $\text{Co}^{\text{III}}\text{W}$  as an acceptor in the presence of water ( $0.50 \text{ mol dm}^{-3}$ ) has already been described above, showing that only the triplet of  $(\text{Bu}')_2\text{NO}^\bullet$  and the triplet of PBN-O $^\bullet$  were detected.

*Photolysis of PBN-Nucleophile in the Presence of 2,4,6-Tri(methoxyphenyl)pyrylium ion as Sensitizer.*—A second viable approach to obtain PBN $^{\bullet+}$  by photolysis is to use a sensitizer (Sens) $^{1e}$  of suitable redox properties according to eqn. (7). The wavelength for excitation is often in the visible



region, and the redox potential can be chosen over a wide range. 2,4,6-Tri(methoxyphenyl)pyrylium ion is an often used sensitizer<sup>14</sup> for which  $E^\circ(\text{Sens}^*/\text{Sens}^-) = 1.98 \text{ V}$  and for which there is a UV maximum of the excitation wavelength at 422 nm and  $\lambda_{\text{max}}$  of fluorescence at 529 nm. Its properties were thus deemed suitable for use as a sensitizer in this context.

However, it turned out that the nucleophiles used above were not all compatible with the sensitizer but reacted with it, most easily seen by the disappearance of the strong fluorescence of the sensitizer and/or colour change and/or precipitation of solid material. Thus triethyl phosphite, fluoride, chloride and acetate failed to give any spin adducts by this method. On the other hand, irradiation with filtered light (cut-off  $< 400 \text{ nm}$ ) of a dichloromethane solution of PBN ( $100 \text{ mmol dm}^{-3}$ ),  $\text{Bu}_4\text{NT}$  ( $80 \text{ mmol dm}^{-3}$ ) and 2,4,6-tri(methoxyphenyl)pyrylium tetrafluoroborate ( $7 \text{ mmol dm}^{-3}$ ) produced a clean spectrum of PBN-T $^\bullet$ , developing with time as shown in Fig. 6. Also, with 3,5-lutidine as the nucleophile the EPR spectrum of the corresponding spin adduct ( $a^N = 1.34 \text{ mT}$ ,  $a^H = 0.23 \text{ mT}$ ,  $a^N = 0.30 \text{ mT}$ ; lit.,<sup>6</sup>  $a^N = 1.34 \text{ mT}$ ,  $A^H = 0.22 \text{ mT}$ ,  $a^N = 0.305 \text{ mT}$ ) was easily obtained.

*Inverse Spin Trapping with 5,5-Dimethylpyrroline 1-Oxide (DMPO)-TBPA $^{\bullet+}$ .*—As stressed above, TBPA $^{\bullet+}$  undergoes electrophilic reactions with nucleophiles with  $E^\circ(\text{Nu}^\bullet/\text{Nu}^-) > 2.0 \text{ V}$ ,<sup>7</sup> such as acetate, cyanide and chloride ion and therefore is

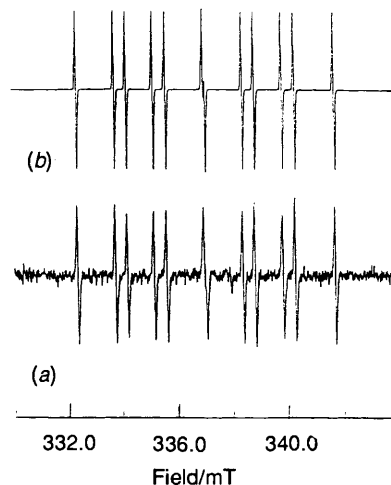


Fig. 7 (a) The EPR spectrum of DMPO-P(OEt) $_3^{\bullet+}$  in dichloromethane and (b) a simulated spectrum using the parameters given in Table 1 (Gaussian lineshape, linewidth 0.05 mT)

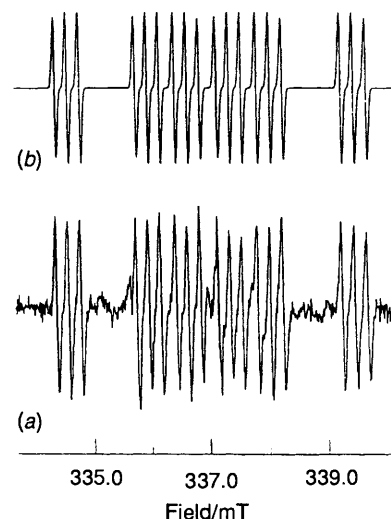


Fig. 8 (a) The EPR spectrum of DMPO-T $^\bullet$  in dichloromethane and (b) a simulated spectrum using the parameters given in Table 1 (Gaussian lineshape, linewidth 0.05 mT)

important for mechanistic delineation of inverted spin trapping. DMPO is the second most employed spin trap after PBN and it was therefore of interest to see whether it engages in inverted spin trapping. DMPO has an anodic peak potential at *ca.* 1.9 V,<sup>1b</sup> about 0.2 V above that of PBN, and thus should be less susceptible to ET oxidation. Its excitation wavelength is 242 nm, about 50 nm lower than that of PBN, and thus in a spectral range where the light intensity of the Hg lamp employed is very low.

Solutions of DMPO and nucleophile in dichloromethane were oxidized by a deficit of TBPA $^{\bullet+}\text{SbCl}_6^-$  as described previously,<sup>6</sup> and the EPR spectra recorded. The results are shown in Table 1, where among others the hfs values of new DMPO adducts with  $(\text{EtO})_3\text{P}^+$  and tetramethylsuccinimidyl, are given; the corresponding EPR spectra are shown in Figs. 7 and 8. Hydrogendiacetate ion gave two signals, one originating from the known<sup>15</sup> carbonylaminoxyl radical ('DMPOOx') and the second from the similarly known<sup>16</sup> acetoxy-DMPO adduct. 3,5-Lutidine gave only the signal originating from DMPOOx. In spite of much effort, the fluoride salt  $\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$  did not produce any DMPO-F $^\bullet$ ; instead a strong hydroxyl adduct signal was obtained on top of a weak, persistent signal of an unidentified three-spin system (1 H,  $2 \times 1 \text{ N}$ , Table 1). The hydroxyl adduct decayed with a half-life of *ca.* 40 min, in good agreement with the published value

**Table 1** Spin adducts from the reaction between  $TBPA^{++}$   $SbCl_6^-$  and DMPO–nucleophile in dichloromethane

| Nucleophile                        | Found    |          |          |                   | Lit.              |                   |                     | Spin adduct from                  |
|------------------------------------|----------|----------|----------|-------------------|-------------------|-------------------|---------------------|-----------------------------------|
|                                    | $a^N/mT$ | $a^H/mT$ | $a^H/mT$ | $a^{Nu}/mT$       | $a^N/mT$          | $a^H/mT$          | $a^{Nu}/mT$         |                                   |
| None                               | 0.68     |          |          | 0.34 <sup>a</sup> | 0.72 <sup>b</sup> |                   | 0.35 <sup>a,b</sup> | O=                                |
| P(OEt) <sub>3</sub>                | 1.43     | 1.86     |          | 4.63              |                   |                   |                     | (EtO) <sub>3</sub> P <sup>+</sup> |
| (AcO) <sub>2</sub> H               | 0.67     |          |          | 0.34 <sup>a</sup> | 0.72 <sup>b</sup> |                   | 0.35 <sup>a,b</sup> | O=                                |
|                                    | 1.28     | 1.04     |          | 0.12              | 1.25              | 1.00              | 0.090               | AcO                               |
| Me <sub>4</sub> -Succinimide       | 1.39     | 2.07     |          | 0.015             |                   |                   |                     | Me <sub>4</sub> succinimido       |
| 3,5-Lutidine                       | 0.67     |          |          | 0.34 <sup>a</sup> | 0.72 <sup>b</sup> |                   | 0.35 <sup>a,b</sup> | O=                                |
| F <sup>-</sup> , 3H <sub>2</sub> O | 1.44     | 2.07     |          | 0.20 <sup>c</sup> |                   |                   |                     | Unknown                           |
|                                    | 1.43     | 1.24     |          |                   | 1.41 <sup>d</sup> | 1.23 <sup>d</sup> |                     | HO                                |

<sup>a</sup> Two hydrogens. <sup>b</sup> In water (ref. 2). <sup>c</sup> 1:1:1 triplet. <sup>d</sup> In acetonitrile (ref. 2).

(ca. 25 min at pH 6 in water).<sup>17</sup> The unidentified spin adduct could not be made by  $TBPA^{++}$  oxidation of a DMPO–tributylamine solution, otherwise a possibility in view of the behaviour of the fluoride salt.<sup>8</sup>

*Inverse spin trapping with DMPO under photolytic conditions.*—The  $Co^{III}W$  method (eqn. 5) did not work with most of the nucleophiles employed above. Only with tetramethylsuccinimide was a weak signal of the spin adduct detectable. With 2,4,6-trianisylpyrylium ion as sensitizer, none of the nucleophiles employed above gave any signal of spin adduct, as expected in view of the PBN results above.

*Inverse Spin Trapping with 3,3,5,5-Tetramethyl-1-pyrroline 1-Oxide (TMPO) and  $TBPA^{++}$ .*—This spin trap has an anodic peak potential of ca. 2.0 V and is thus slightly more difficult to oxidize than DMPO. Attempts to detect spin adducts by  $TBPA^{++}$  oxidation of TMPO–nucleophile solutions in dichloromethane, using the same nucleophiles as in Table 1, gave a positive result only for triethyl phosphite ( $a^N = 1.41$  mT,  $a^H = 1.74$  mT,  $a^P = 4.59$  mT) whereas for the others, a signal due to, what is most likely,  $TMPOOx$  ( $a^N = 0.65$  mT, cf.  $a^N$  for other carbonylaminoxyls:  $PBNOx$  0.80,  $DMPOOx$  0.67 mT) was the only significant one.

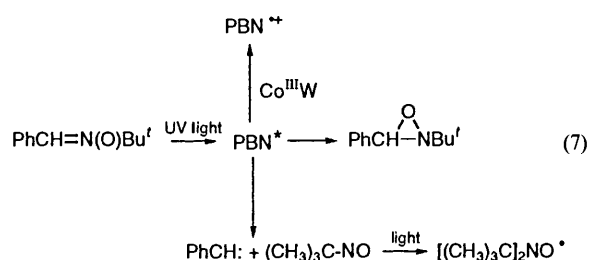
## Discussion

*Photochemical Initiation.*—The aim of this series of papers is to provide evidence for inverted spin trapping under conditions which unequivocally exclude the operation of the normal mechanism and/or the nucleophilic addition/oxidation scheme of eqn. (2). This was achieved in the case of PBN under thermal conditions by suitable combinations of oxidant and nucleophile, known<sup>6,7</sup> or theoretically predicted<sup>8</sup> not to undergo electron transfer within themselves.

As the results reported above indicate, and as discussed below, such evidence is not as clear cut in the case of photochemical generation of spin adducts. The first approach taken here, to excite the spin trap photochemically and oxidize the excited state by a weak oxidant, in itself incapable of oxidizing the spin trap or the nucleophile [eqn. (5)], in order to generate the radical cation of the spin trap, is presumably the best one can achieve. It is also analogous to experimental procedures employed in the past for spin-trapping studies, such as photolysis of spin trap/nucleophiles in the presence of hydrogen peroxide, peroxydisulfate, etc. The second approach, to use a sensitizer to oxidize the spin trap, is also viable but at least with the one chosen initially, compatibility problems became evident and made certain experiments impossible.

Experiments designed to establish the fate of PBN itself under photochemical conditions in dichloromethane showed that photolysis with filtered light (cut off < 435 nm) did not give any EPR-active products (Fig. 1). With unfiltered light the

production of di(*tert*-butyl)aminoxyl was rapid, indicating that  $PBN^*$  has a minor cleavage pathway to *tert*-butyl-NO available and thus to di(*tert*-butyl)aminoxyl,<sup>1b</sup> in addition to the known cyclization reaction to give an oxaziridine [eqn. (7)].<sup>11</sup> In the presence of  $Co^{III}W$ , the production of di(*tert*-



butyl)aminoxyl was slower (Fig. 1), as expected if  $PBN^*$  is diverted to  $PBN^{++}$  by oxidation.

Addition of water to the system led to the formation of  $PBNOx$ , a species which in all probability is formed by trapping of  $PBN^{++}$  by water to give  $PBN-OH^+$ , which is further oxidized to  $PBNOx$  by  $Co^{III}W$  by an ECE-type mechanism.<sup>6</sup> It is well known that substitution of OH into radicals [like the series  $(CH_3)_3C^{\cdot} \sim 0.3$  V,  $HO(CH_2)_2C^{\cdot} - 0.9$  V, 2-methyl-1,3-dioxolan-2-yl  $-0.95$  V]<sup>18</sup> makes them much better electron donors.

With triethyl phosphite as a nucleophile, the scheme of eqn. (5) seemingly worked well (Fig. 2), but the ready production of  $PBN-P(OEt)_3^{++}$  with unfiltered light even in the absence of  $Co^{III}W$ , raises several problems. Even if oxaziridines have been described as resistant toward reaction with nucleophiles in the sense of eqn. (6),<sup>19</sup> it cannot be excluded that a strong nucleophile like triethyl phosphite might react in this fashion. However, check experiments in which the oxaziridine had been pregenerated by photolysis of PBN, showed that this type of reaction does not occur. Since triethyl phosphite cannot act as an electron acceptor (reduced at a potential <  $-2.2$  V),<sup>20</sup> the possibility remains that it might act as a sensitizer. It has a very weak UV spectral maximum at ca. 290 nm that might be photoactive under the concentration conditions employed. It is also possible that dichloromethane might act as the acceptor of eqn. (5), but the formation of  $PBN-P(OEt)_3^{++}$  must then additionally be explained by the high nucleophilicity of triethyl phosphite and the chemical stability of the spin adduct. None of the other nucleophiles tried reacted with only dichloromethane as acceptor.

All other nucleophiles (hydrogenacetate, fluoride, chloride, cyanide, tetramethylsuccinimide) conform with expectations based on eqn. (5), at least as long as the reactions are carried out in dichloromethane: there was no production of the appropriate spin adduct with filtered light, but immediate onset of its production upon removal of the filter. However,

now the nucleophilic addition/oxidation pathway in some cases becomes of some concern. In  $\text{CDCl}_3$  (used because of its freedom from ethanol as stabilizer) this mechanism was demonstrated for fluoride ion and tetramethylsuccinimide, the two strongest bases of the list above. Evidently the lower relative permittivity of  $\text{CDCl}_3$ , 4.8 as compared with that of dichloromethane, 8.9, forces the initial equilibrium of eqn. (2) to the right and makes the hydroxylamine oxyanion available for oxidation by dioxygen or  $\text{Co}^{\text{III}}\text{W}$ .

The sensitizer mechanism [eqn. (7)] worked with nucleophiles (tetramethylsuccinimide, 3,5-lutidine) which were compatible with the sensitizer, 2,4,6-tri(methoxyphenyl)pyrylium ion. In this case, light with  $\lambda > 400$  nm was used in order to excite at the 422 nm UV spectral maximum.

**DMPO and TMPO in Inverted Spin Trapping.**—These spin traps are more difficult to oxidize than PBN by 0.2–0.3 V, at least as judged by anodic peak potentials in cyclic voltammograms (PBN, 1.74; DMPO, 1.92 and TMPO, 2.02 V in acetonitrile–tetrabutylammonium hexafluorophosphate). Even with a strong oxidizing agent, like hexachloroosmate(v), it has already been established<sup>8</sup> that such a potential difference reduces the incidence of inverted spin trapping from a defined list of nucleophiles. Thus for DMPO only hydrogendiacetate, tetramethylsuccinimide and triethyl phosphite engaged in spin-adduct formation with  $\text{TBPA}^{++}$  as the oxidant, whereas fluoride ion gave the hydroxyl adduct, presumably *via* reaction between  $\text{DMPO}^+$  and water available from the hydration shell of fluoride ion. TMPO was even less reactive in its reactions with nucleophile/ $\text{TBPA}^{++}$  and gave a positive result only with triethyl phosphite, the strongest nucleophile on the list. In this case it is also probable that steric hindrance makes itself felt in the neopentyl-like situation around the 2-carbon of TMPO.

Under photolytic conditions, the scheme of eqn. (5) worked only for DMPO–tetramethylsuccinimide, probably because excitation of DMPO takes place outside the available wavelength range of the lamp used. The sensitizer method did not work.

## Experimental

**Materials.**—For most compounds used here, see refs. 6 and 8 for details. DMPO and TMPO were obtained from Aldrich. Tetrabutylammonium 12-tungstocobaltate(III) was available from an earlier study.<sup>9</sup> 2,4,6-Tri(methoxyphenyl)pyrylium tetrafluoroborate was a gift from Professor Eberhard Steckhan, Bonn University.<sup>14</sup>

**Reactions.**—Reactions with tris(4-bromophenyl)aminium hexachloroantimonate were carried out as described.<sup>6</sup> Photolyses were performed in the photolysis cavity of the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. The UV lamp was the 50 W high-pressure Hg lamp from Bruker (ER 202), in appropriate cases equipped with a filter of suitable cut-off. The experiments of Figs. 1–6 were run by the automation routine.

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