Inverted Spin Trapping. Part IV.† Application to the Formation of Imidyl Spin Adducts from *N*-Haloimides

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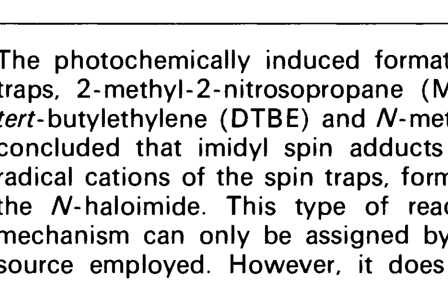
The photochemically induced formation of imidyl spin adducts from *N*-haloimides and four spin traps, 2-methyl-2-nitrosopropane (MNP), *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN), 1,1-di-*tert*-butylethylene (DTBE) and *N*-methylene-*tert*-butylamine *N*-oxide (MBN) has been studied. It is concluded that imidyl spin adducts from MNP, PBN and MBN are most likely formed *via* the radical cations of the spin traps, formed by reaction between the excited state of the spin trap and the *N*-haloimide. This type of reaction is a case of inverted spin trapping. For DTBE, this mechanism can only be assigned by analogy, since this molecule cannot be excited by the light source employed. However, it does form imidyl adducts by chemical or photosensitized (using 2,4,6-trianisylpyrylium ion or 9,10-dicyanoanthracene as the sensitizer) oxidation of DTBE solutions containing succinimidate anions, so even in this case inverted spin trapping cannot be excluded.

The phenomenon of spin trapping is defined as the reaction of a radical $R^\bullet$ with a spin trap ST with formation of a persistent spin adduct, which can be studied primarily by EPR spectroscopy [eqn. (1)].[1] Examples of spin traps are shown below; they are

$$\mathrm{ST} + \mathrm{R}^\bullet \longrightarrow \mathrm{R{-}ST}^\bullet \qquad (1)$$

normally nitroso compounds or aminoxyls, but sterically hindered alkenes can also be used. An important problem in spin trapping chemistry is the study of redox processes, as for example oxidation of a mixture of ST and a nucleophile Nu^- by an oxidant in the hope of gaining support for the intervention of $\mathrm{Nu}^\bullet$ by observing $\mathrm{Nu{-}ST}^\bullet$ [eqn. (2)]. Many such studies have


MNP PBN DTBE MBN

$$\mathrm{Nu}^- \xrightarrow{-e^-} \mathrm{Nu}^\bullet \xrightarrow{\mathrm{ST}} \mathrm{Nu{-}ST}^\bullet \qquad (2)$$

been performed by chemical, photo- or electro-chemical or enzymic oxidation and in most cases the mechanism of eqn. (2) has been assumed to be valid. However, in a number of cases[2] a different mechanism was proposed, namely initial oxidation of ST to its radical cation, followed by reaction with Nu^- [eqn. (3)]. This mechanism was recently placed on a firm ground and

$$\mathrm{ST} \xrightarrow{-e^-} \mathrm{ST}^{\bullet+} \xrightarrow{\mathrm{Nu}^-} \mathrm{Nu{-}ST}^\bullet \qquad (3)$$

denoted inverted spin trapping[3–5] because of the inverted electron configuration of the reagent pair, $\mathrm{Nu}^-/\mathrm{ST}^{\bullet+}$ *vs.* $\mathrm{Nu}^\bullet/\mathrm{ST}$ [eqns. (2) and (3)].

It should be stressed that the use of photochemical generation procedures is particularly prone to diverting spin trapping chemistry to its inverted variety. Excited states are normally strong electron donors toward any acceptors present and *vice versa*,[6] and situations where the excited state of the spin trap might reduce a weak acceptor (A) and thus result in the formation of $\mathrm{ST}^{\bullet+}$, are easily realized [eqn. (4)].[5] This was

$$\mathrm{ST} \xrightarrow{h\nu} \mathrm{ST}^* \xrightarrow{\mathrm{A}} \mathrm{ST}^{\bullet+} \xrightarrow{\mathrm{Nu}^-} \mathrm{Nu{-}ST}^\bullet \qquad (4)$$

demonstrated for a photochemical model reaction involving *N*-benzylidene-*tert*-butylamine *N*-oxide (PBN, see above), nucleophile, and the weak oxidant $(\mathrm{Bu_4N})_5\mathrm{Co^{III}W_{12}O_{40}}$ in dichloromethane.[5] Among several other nucleophiles, succinimide anions worked quite well in the photochemical version of inverted spin trapping, as they also did in systems with chemical oxidants.[3,4] Also, sensitized photooxidation of PBN was possible.

Imidyl spin trapping has previously been observed from the photolysis of a solution of a spin trap and an *N*-haloimide (denoted Im–X; X is Br or Cl, Im usually succin-, glutar- or phthal-imidyl). In this way, imidyl spin adducts were formed from 2-methyl-2-nitrosopropane (MNP)[7,8,9b] and 1,1-di(*tert*-butyl)ethylene (DTBE),[9] whereas *N*-methylene-*tert*-butylamine *N*-oxide (MBN)[8] gave the imidyl adduct even in the dark. Curiously, no imidyl spin adduct was obtained from PBN.[8] Since *N*-bromosuccinimide (denoted SBr in the following) and *N*-chlorosuccinimide (SCl) both are weak electron acceptors, with $E^\circ(\mathrm{SX/SX^{\bullet-}})$ in the range 0–0.3 V,[10,11] photochemical reactions according to eqn. (4), with A = Im–X, should be feasible. Other novel and pertinent facts about imidyl systems are the differing cleavage modes of the radical anions of SBr[12] and SCl[11] [eqns. (5) and (6)] and the high redox potential of

$$\mathrm{SBr} + e^- \longrightarrow \mathrm{SBr}^{\bullet-} \longrightarrow \mathrm{S}^- + \mathrm{Br}^\bullet \qquad (5)$$

$$\mathrm{SCl} + e^- \longrightarrow \mathrm{SCl}^{\bullet-} \longrightarrow \mathrm{S}^\bullet + \mathrm{Cl}^- \qquad (6)$$

$\mathrm{S}^\bullet$,[11] $E^\circ(\mathrm{S^\bullet/S^-})$ being 2.2 V in aqueous medium. The rate constant of ring-opening of $\mathrm{S}^\bullet$ [eqn. (7)] was found to be

$$\mathrm{S}^\bullet \longrightarrow \mathrm{OCNCOCH_2CH_2}^\bullet \qquad (7)$$

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† Part III, see ref. 5.

Table 1 Redox properties of spin traps, *N*-haloimides and sensitizers

ST	$E(ST^{\cdot+}/ST)$/V	$E(ST/ST^{\cdot-})$/V	λ_{exc}/nm (log ε/dm^3 mol^{-1} cm^{-1})	$E(ST^{\cdot+}/ST^*)$/V as reductant[a]	$E(ST^*/ST^{\cdot-})$/V as oxidant[b]
MNP	2.06[c]	−1.53[c]	676	0.27	0.36
MNP	2.08[c]	−1.53[d]	676	0.26	0.29
PBN	1.71[c]	−2.16[c]	298	−2.46	2.01
DTBE	1.84	< −2.8	185[e]	−4.83	3.87
MBN	1.9	−1.7	*ca.* 250	−3.0	3.2
SBr	*ca.* 2.5	0.3[f]	202 (4.13)	−3.6	6.4
			308 (1.0)	−1.5	4.3
SCl	*ca.* 2.5	0.3[g]	198 (4.07)	−3.7	6.5
			263 (1.0)	−2.2	5.0
GluBr	*ca.* 2.5	0.3[g]	208 (4.13)	−3.4	6.2
			332 (1.0)	−1.2	4.0
GluCl	*ca.* 2.5	0.3[g]	204 (4.08)	−3.5	6.3
			279 (1.0)	−1.9	4.7
TBr	*ca.* 2.5	0.3[g]	204 (4.05)	−3.5	6.3
			318 (1.0)	−1.4	4.2
PBr	*ca.* 2.5	0.3[g]	220 (4.68)	−3.1	5.9
			294 (3.64)	−1.7	4.5
			350 (1.0)	−1.0	3.8
TAP[h]		−0.36	529 (2.84)		1.98
9,10-DCA[i]	3.10	−0.65	440	0.3	2.15
CCl_4		−0.6[j]	250 (1.0)		4.3

[a] Estimated from the equation $E(ST^{\cdot+}/ST^*) = E°(ST^{\cdot+}/ST) - \Delta E_\lambda$, where ΔE_λ is the energy of the light employed (ref. 14). [b] Estimated from the equation $E(ST^*/ST^{\cdot-}) = E°(ST/ST^{\cdot-}) + \Delta E_\lambda$, where ΔE_λ is the energy of the light employed (ref. 14). [c] Ref. 15. [d] Ref. 16. [e] Ref. 17. [f] Kinetically determined $E°$ value (see ref. 10). [g] Put equal to $E°(SBr/SBr^{\cdot-})$. [h] Ref. 18. The wavelength given corresponds to the triplet excitation energy. [i] Ref. 19. [j] Kinetically determined $E°$ value (see ref. 20).

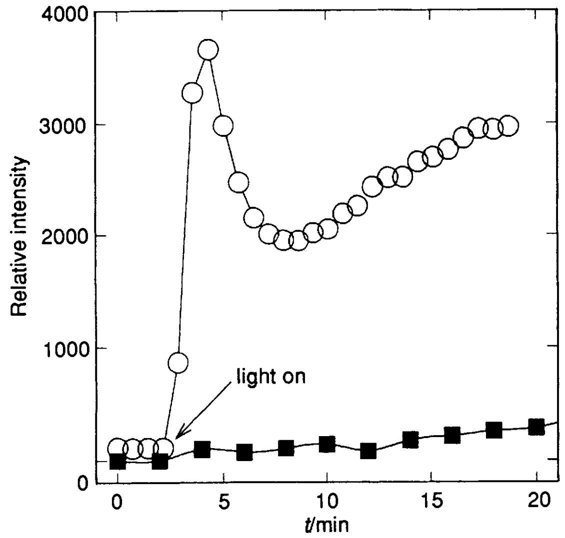

Fig. 1 Time dependence of the S–MNP' EPR signal in a solution of SBr and MNP in dichloromethane without (■) and with irradiation (○; filter with cut-off < 530 nm; start of illumination after 2 min). The points are joined by lines only to improve readability.

8×10^4 s^{-1} in water, in reasonable agreement with one published value[13a] in an organic solvent but several powers of ten smaller than other proposed values.[13b] With these developments in mind, it was of interest to reinvestigate some aspects of imidyl spin trapping to see whether inverted spin trapping might be involved. In what follows, it is shown that the photoinduced formation of imidyl spin adducts is strongly influenced by the redox properties of the species involved, and that the radical cations of spin traps are likely to be involved in most, if not all, imidyl spin trappings observed.

Results and Discussion

Redox Properties of Spin Traps, N*-Haloimides and Sensitizers.*—Table 1 summarizes the redox properties of the ground and excited states of the spin traps, *N*-haloimides and sensitizers used in this investigation. Some values were available from the literature, and the remaining ones were determined by cyclic voltammetry in CH_3CN–tetrabutylammonium hexafluorophosphate (0.2 mol dm^{-3}). The values given are reported as anodic or cathodic peak potentials due to the electrochemical irreversibility of most systems.

The haloimides showed elongated, vaguely defined oxidation peaks around 2.5 V *vs.* NHE (normal hydrogen electrode; all potentials given in this paper are referred to this electrode) upon anodic oxidation. On the return scan, the bromoimides displayed a peak at about 1.1 V due to reduction of bromine liberated in the process at 2.5 V. $E°(SBr/SBr^{\cdot-})$ was determined by an indirect kinetic method in acetonitrile in a previous study[10] and it was assumed that the other haloimides can be assigned the same value, 0.3 V (based on their similar kinetic behaviour toward donor molecules of the ferrocene type).[21] *N*-Haloimides possess a strong UV band around 200 nm, meaning that their excited states come out as extremely strong oxidants, E°_{red} around 6 V (!), and reductants, $E^\circ_{ox} \approx -3.5$ V. In order to indicate the width of these bands, Table 1 also gives the wavelength at which ε attains the value of *ca.* 10, corresponding to an *N*-haloimide absorbance of 0.1–0.2 at the actual experimental concentration, and the redox properties of the excited state at this wavelength.

1,1-Di-*tert*-butylethylene had a fairly low E_{pa}, 1.84 V, in agreement with the general behaviour of sterically strained alkenes.[22]

Trapping of Imidyls by MNP.—The first EPR spectral sightings of trapped imidyl radicals, triplets of triplets, a^N = 1.64 and $a^{N'}$ = 0.181 mT, were obtained by photolysis of *N*-haloimides in the presence of MNP.[7,8,9b] It was suggested that homolytic cleavage of the excited Im–X gives Im' and X' followed by trapping of Im' by MNP. Repetition of these experiments established that (*i*) there was slow formation of the spin adduct in the dark which led to a gradual increase of the intensity of the signal over many hours, and (*ii*) light with cut-off < 530 nm was responsible for the photolytic generation of the spin adduct (see also ref. 8), as shown in Figs. 1 and 2 for

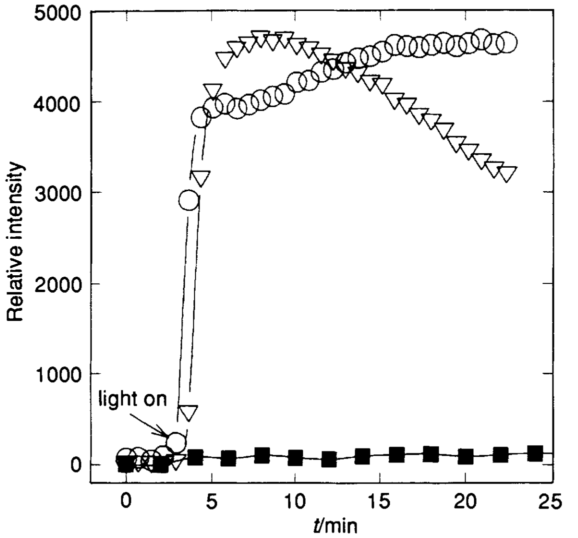

Fig. 2 Time dependence of the Im–MNP$^{\bullet}$ EPR signal in a solution of Im–Cl and MNP in dichloromethane without (SCl; ■) and with irradiation (SCl, ○; GluCl, ▽; filter with cut-off < 530 mn; start of illumination after 2 min). The points are joined by lines only to improve readability.

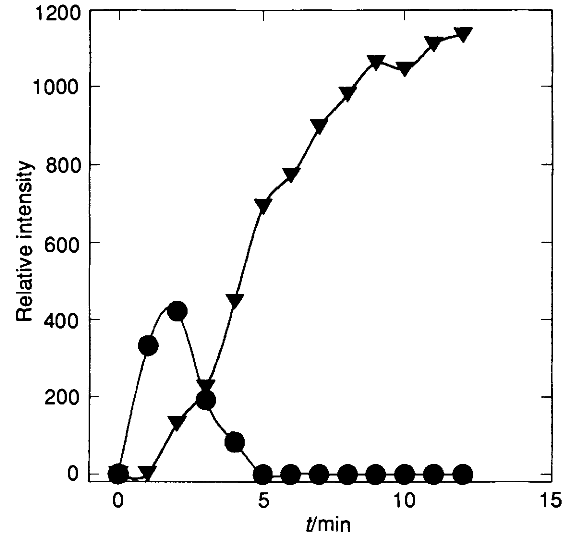

Fig. 3 Time dependence of the Cl–PBN$^{\bullet}$ (●) and S–PBN$^{\bullet}$ EPR signals (▼) in a solution of SCl and PBN in $CDCl_3$ under irradiation with unfiltered UV light. The points are joined by lines only to improve readability.

SBr, SCl and GluCl (*N*-chloroglutarimide). After onset of the irradiation, the signal increased in intensity by a factor of 40–50 within 2 min. Thus it appears that MNP* must be the species initiating the formation of the spin adduct, most likely *via* eqns. (8) and (9) which represent cases of eqn. (4) behaviour.

$$\mathrm{MNP} \xrightarrow{h\nu} \mathrm{MNP}^{*} \xrightarrow{\mathrm{Im\text{–}Br}} \mathrm{MNP}^{\bullet +} + \mathrm{Im}^{-} + \mathrm{Br}^{\bullet} \longrightarrow \mathrm{MNP\text{–}Im}^{\bullet} \quad (8)$$

$$\mathrm{MNP} \xrightarrow{h\nu} \mathrm{MNP}^{*} \xrightarrow{\mathrm{Im\text{–}Cl}} \mathrm{MNP}^{\bullet +} + \mathrm{Im}^{\bullet} + \mathrm{Cl}^{-} \longrightarrow \mathrm{MNP\text{–}Cl}^{\bullet} \quad (9)$$

$$\mathrm{MNP\text{–}Cl}^{\bullet} \xrightarrow{\mathrm{Im}^{-}} \mathrm{MNP\text{–}Im}^{\bullet}$$

The spin trap is promoted to its excited state, for MNP with $E(\mathrm{MNP}^{\bullet +}/\mathrm{MNP}^{*}) = 0.26$ V, and this is capable of reducing Im–X in a very fast step. In the case of Im–Br, this mechanism leads directly to an $\mathrm{MNP}^{\bullet +}$ Im^{-} ion pair which collapses to the spin adduct. The alternative mechanism,[8] that Bu^{t}NO* decomposes to NO and *tert*-butyl radical which then abstracts a bromine atom from SBr to give S$^{\bullet}$, is deemed less likely, since no trace was seen of $(\mathrm{Bu}^t)_2\mathrm{NO}^{\bullet}$, the characteristic product of MNP photolysis.[1b]

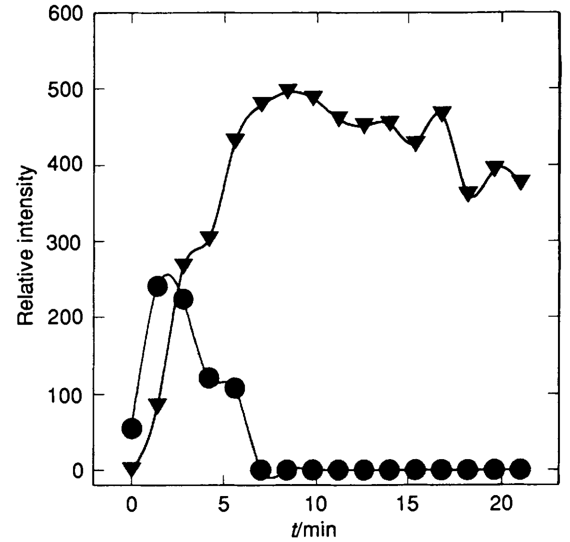

Fig. 4 Time dependence of the Cl–PBN$^{\bullet}$ (●) and Glu–PBN$^{\bullet}$ EPR signals (▼) in a solution of GluCl and PBN in $CDCl_3$ under irradiation with unfiltered UV light. The points are joined by lines only to improve readability.

For Im–Cl, the radical anion of which has the opposite cleavage mode [eqn. (6)], it is not immediately obvious how the spin adduct is formed. The first spin adduct in eqn. (9) should be MNP–Cl$^{\bullet}$ which, however, has never been detected,[1d] presumably because of its expected high reactivity toward nucleophilic species. This type of reactivity was recently[23] demonstrated for spin adducts of type ST–Hal$^{\bullet}$, $\mathrm{ST\text{–}OSO_3}^{\bullet -}$, $\mathrm{ST\text{–}OPO_3H}^{\bullet -}$, *etc*. In the case of eqn. (9), any MPN–Cl$^{\bullet}$ formed would react rapidly with ImH/Im^{-} formed by further H abstraction/redox transformations of Im$^{\bullet}$ and thus give MNP–Im$^{\bullet}$. This seems to be the pathway for formation of the imidyl spin adduct from SCl–PBN (see below) where both the chloro and imidyl spin adducts can be successively detected during the course of the photolysis reaction. The mechanism of eqn. (9) is suggested on the basis of this analogy, but we cannot exclude that the imidyl radical is trapped properly by MNP, or *via* an initial electron transfer between S$^{\bullet}$ and MNP, always a possibility for an exergonic redox step.[24]

Trapping of Imidyls by PBN.—Initial experiments in which SCl and PBN were photolysed (Hg lamp, no filter) in dichloromethane or acetonitrile showed that the characteristic signal of PBN–Cl$^{\bullet}$ appeared during the first 1–1.5 min of irradiation, but that this signal was rapidly (next few min) replaced by that of PBN–S$^{\bullet}$ (EPR parameters, see ref. 3), in line with the mechanism of eqn. (9), Im = S. The same behaviour was seen in $CDCl_3$, although on a longer timescale, as shown in Fig. 3 for SCl and Fig. 4 for GluCl (*N*-chloroglutarimide; for Glu–PBN$^{\bullet}$ the following EPR parameters were found: $a^{\mathrm{N}} = 1.44$, $a^{\mathrm{H}} = 0.735$, $a^{\mathrm{N}'} = 0.135$ mT). The reaction occurred also with filtered light with cut-off at 295 nm, by which only PBN can be excited (Table 1). With benzene as the solvent, a strong signal of PBN–Cl$^{\bullet}$ was built up from both SCl and GluCl and persisted for at least 30 min of photolysis. No signal from the imidyl adduct was detectable during these runs. The PBN–Cl$^{\bullet}$ signal decayed slowly (10–15 min) after discontinuation of the photolysis, being replaced by the triplet ($a^{\mathrm{N}} = 0.80$ mT) due to PHCON(O$^{\bullet}$)Bu^t. The presence of $\mathrm{Bu_4NS}$ during the benzene photolysis quenched the Cl–PBN$^•$ signal and caused the S–PBN$^•$ signal to appear, as expected.

We interpret these results as follows. PBN* is formed by excitation of PBN at 296 nm (Table 1) and reduces Im–Cl with formation of the triad PBN$^{•+}$ Im$^•$ Cl$^-$ from which PBN–Cl$^•$ is initially formed. Im$^•$ will give ImH by hydrogen-atom abstraction from the solvent, thus supplying a nucleophilic species to replace chlorine in PBN–Cl$^•$ and give PBN–Im$^•$. Im$^•$ might in principle also add directly to PBN, but in such a case it is difficult to see why the reaction sequence chlorine adduct→imidyl adduct should be seen so clearly; both species would be expected to grow in parallel. In benzene, Im$^•$ is instead trapped by benzene[25] and PBN–Cl$^•$ will persist for a relatively long time owing to the unavailability of nucleophilic species other than chloride ion and spurious water. An added nucleophile, like S$^-$, will either replace the chlorine atom in Cl–PBN$^•$ or react directly with PBN$^{•+}$.

Photolysis of SBr–PBN in dichloromethane or $CDCl_3$ gave no PBN–S$^•$, as found before.[8] However, since SBr and *N*-bromoimides in general would produce some bromine by coupling of the bromine atoms formed according to eqn. (5) and/or reaction of HBr (formed by H abstraction by Br$^•$ from solvent molecules) with SBr,[26] the rather strong oxidant, bromine, would be available for further oxidation of any PBN–S$^•$ formed to PBN–S$^+$. Thus addition of a bromine trap should eliminate this possibility.

Irradiation of SBr–PBN in dichloromethane in the presence of phenylacetylene gave a medium-intensity signal from PBN–S$^•$ and triplet of doublets ($a^N = 1.44$ and $a^H = 0.302$ mT) of about equal intensity. The time evolution of these signals is shown in Fig. 5. Thus the presence of a bromine trap removed the bromine formed and allowed for PBN–S$^•$ to build up to detectable concentrations. The 3 × 2 signal presumably originates from trapping of 2-bromo-1-styryl radical, formed by reaction of Br$^•$ with phenylacetylene. This mode of formation would be dictated by the electron-transfer step of eqn. (8) which liberates a bromine atom for attack at the alkyne.

Similar behaviour was found when SBr–PBN was photolysed in dichloromethane with cyclohexene present. A strong PBN–S$^•$ signal was obtained, accompanied by a weaker 3 × 2 signal of $a^N = 1.40$ and $a^H = 0.203$ mT, the latter assigned to the PBN adduct of 2-bromocyclohexyl radical formed in the same way as above.

A further test of the origin of the 3 × 2 signals could be performed by photolysing PBN together with *N*-bromoglutarimide (GluBr) or *N*-bromotetramethylsuccinimide (TBr). Apart from the Glu–PBN$^•$ signal, GluBr–PBN in the presence of phenylacetylene or cyclohexene gave the same 3 × 2 signal as found from the SBr experiments, $a^N = 1.40$ and $a^H = 0.205$ mT or $a^N = 1.46$ and $a^H = 0.31$ mT, respectively. From TBr–PBN strong signals of T–PBN$^•$ ($a^N = 1.43$, $a^H = 0.516$, $a^{N'} = 0.129$ mT)[3] were obtained in addition to 3 × 2 signals, with phenylacetylene present of $a^N = 1.45$ and $a^H = 0.30$ mT and with cyclohexene present of $a^N = 1.42$ and $a^H = 0.203$ mT. Since the same EPR parameters were obtained from three different *N*-bromoimides, the 3 × 2 signals must originate from incorporation of the alkyne/alkene in the spin adduct, most likely *via* initial addition of a bromine atom from eqn. (8).

Trapping of Imidyls by DTBE.—This spin trap has widely differing UV spectral properties from the others employed here, in that it cannot be excited by the UV light source. It is oxidized at a fairly low potential, 1.84 V (Table 1), no doubt due to the relief of strain caused by proceeding from the neutral molecule to the radical cation. It was therefore necessary first to establish whether DTBE would undergo inverted spin trapping by sensitized photooxidation with a succinimidate anion (S$^-$ or T$^-$) present.

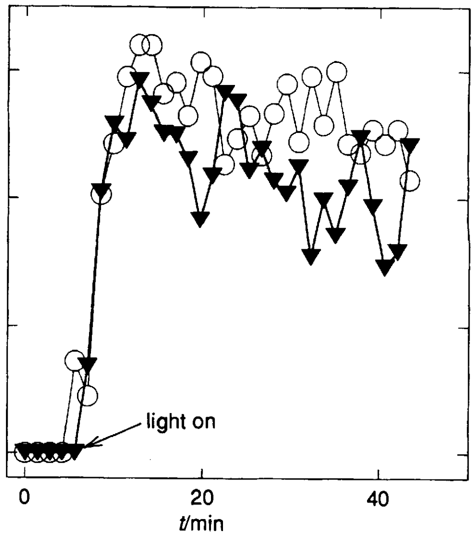

Fig. 5 Time dependence of the S–PBN$^•$ (○) and BrCH=CH(Ph)–PBN$^•$ EPR signals (▼) in a solution of SBr, PBN and phenylacetylene in dichloromethane under irradiation with unfiltered UV light. The points are joined by lines only to improve readability.

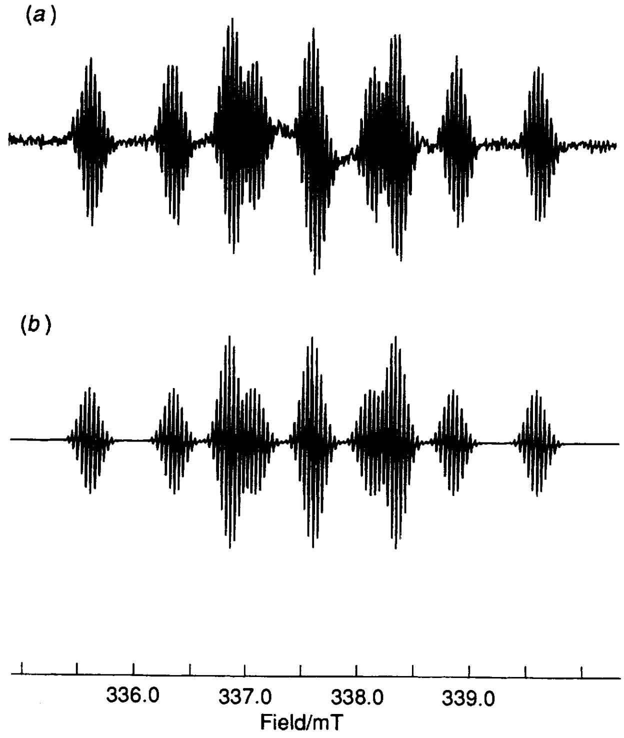

Fig. 6 (*a*) EPR spectrum of T–DTBE$^•$ obtained by irradiation (cut-off < 430 nm) of a solution of DTBE, Bu_4NT and TAP; (*b*) simulated spectrum, using $a^N = 0.74$, $a^{H(18)} = 0.039$ and $a^{H(2)} = 1.25$ mT; Lorentzian lineshape and linewidth 0.015 mT

It was earlier shown[5] that PBN can be photooxidized by the excited state of 2,4,6-trianisylpyrylium ion (TAP) in the presence of Bu_4NT, giving rise to T–PBN$^•$. The same reaction was possible with DTBE–Bu_4NT, using light with cut-off < 430 nm which can only excite the sensitizer. The spectrum of T–DTBE$^•$ is shown in Fig. 6(*a*); it is well simulated by $a^N = 0.74$, $a^{H(2)} = 1.25$ and $a^{H'(18)} = 0.039$ mT [Fig. 6(*b*)]. This signal lasted only during 3–4 min of irradiation, probably due to the slow destruction of TAP by the nucleophile. This phenomenon has been noticed earlier.[5]

The same electrophilic reactivity of TAP must underlie the failure to observe S–DTBE$^•$ from the photolysis (cut-off < 430 nm) of DTBE–Bu_4NS in the presence of this sensitizer. Use of

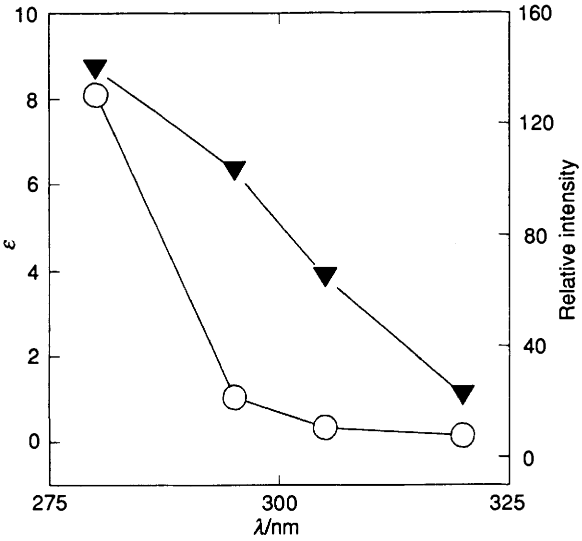

Fig. 7 The intensity of the EPR signal of Glu–DTBE$^{\bullet}$ (▼, right ordinate axis) as a function of filter cut-off. The left ordinate axis shows ε of GluCl (○).

a chemically less sensitive sensitizer, 9,10-dicyanoanthracene (9,10-DCA), gave the known[9] signal of S–DTBE$^{\bullet}$ under the same conditions as for TAP. Also, the T–DTBE$^{\bullet}$ signal was easily produced by this sensitizer.

The published procedure[9] for obtaining imidyl spin adducts from DTBE involved photolysis (UV light) of solutions of Im–Cl and DTBE in various solvents, CD_3CN being used in this particular study because of restrictions imposed by the chemistry involved. We have used dichloromethane since this solvent has been used in most of the inverted spin trapping studies[3–5] and worked as well as CD_3CN in the cases where comparison was made. A repetition of the published procedure with GluCl–DTBE in dichloromethane, using unfiltered UV light gave, after a few min of irradiation, the characteristic signal of Glu–DTBE$^{\bullet}$ identical with that reported.[9] This signal required continuous irradiation in order to be detectable;[9a] it disappeared within seconds after the light had been extinguished. At −50 °C, Glu–DTBE$^{\bullet}$ decayed with a rate constant of 1.9 min^{-1}, whereas S–DTBE$^{\bullet}$ was more stable kinetically, disappearing with a rate constant of 0.36 min^{-1} at −20 °C. Experiments with filtered light showed that light with cut-off at < 320 nm just barely produced an EPR signal (Fig. 7) and at lower wavelengths the signal intensity increased, approximately trailing the tail of the GluCl absorption band at 204 nm. Experiments run with SCl–DTBE under the same conditions gave similar results.

Several attempts were made to detect the chloro spin adduct of DTBE in benzene, in analogy with the results obtained from PBN–SCl photolysis in this solvent (see above). However, no EPR signal whatsoever appeared in benzene runs, nor could Cl–DTBE$^{\bullet}$ be generated by photolysis of *tert*-butyl hypochlorite–DTBE in dichloromethane.

The photolysis of SCl–DTBE in carbon tetrachloride gave initially a medium-intensity signal of S–DTBE$^{\bullet}$ which slowly decayed and was replaced by a 1:2:1 triplet with $a^{H(2)} = 1.07$ mT [see Fig. 8(*a*)]. Each major line was further split into about 30 visible lines with a splitting of 0.020 mT. Since an identical, intense EPR spectrum (Fig. 9) was obtained by photolysis of DTBE alone in carbon tetrachloride, we assign this signal to the known trichloromethyl adduct of DTBE.[27a] GluCl–DTBE behaved in the same way [Fig. 8(*b*)] and exactly the same spectrum as in Fig. 9 was obtained.

In principle, these results can be interpreted in two ways. It is obvious that excitation of Im–Cl is required for formation of Im–DTBE$^{\bullet}$, but what are the further steps of the mechanism?

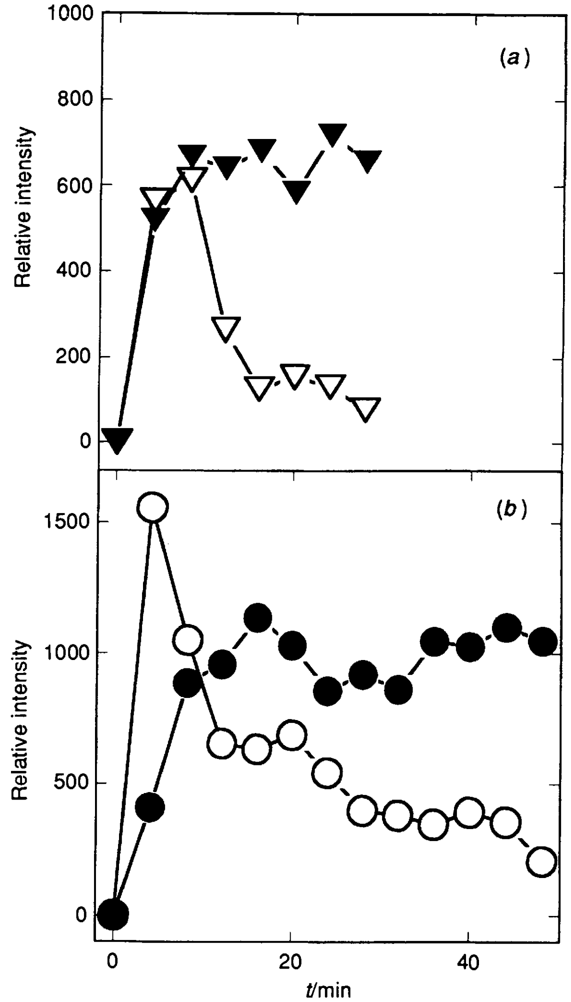

Fig. 8 (*a*) Time dependence of the S–DTBE$^{\bullet}$ (▽) and Cl_3C–DTBE$^{\bullet}$ (▼) EPR signals in a solution of SCl and DTBE in CCl_4 under irradiation with unfiltered UV light; (*b*) same for GluCl–DTBE; Glu–DTBE$^{\bullet}$ (○) and Cl_3C–DTBE$^{\bullet}$ (●)

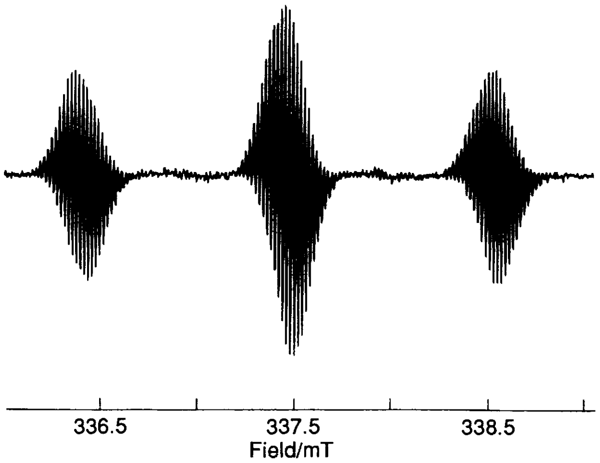

Fig. 9 EPR spectrum of Cl_3C–DTBE$^{\bullet}$ obtained by irradiation of a solution of DTBE in carbon tetrachloride with unfiltered UV light

One can either assume that Im–Cl* dissociates homolytically into Im$^{\bullet}$ and Cl$^{\bullet}$ and that the imidyl is properly trapped by DTBE, or that Im–Cl* oxidizes DTBE to DTBE$^{\bullet+}$ which reacts with Cl^- in the same way as PBN$^{\bullet+}$ does, followed by nucleophilic attack by ImH–Im$^-$ [see above and eqn. (9)]. Cl–DTBE$^{\bullet}$ has been detected in trapping experiments but

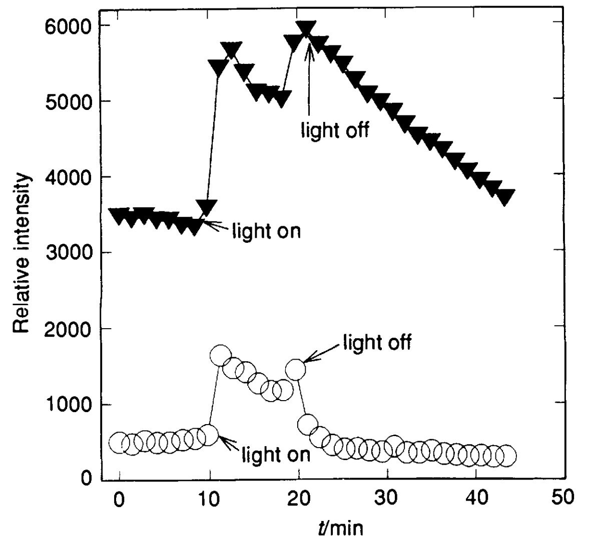

Fig. 10 Time dependence of the S–MBN• (○) and T-MBN• EPR signals (▼) in a solution of SBr or TBr and MBN in dichloromethane in the dark and under illumination (unfiltered UV light)

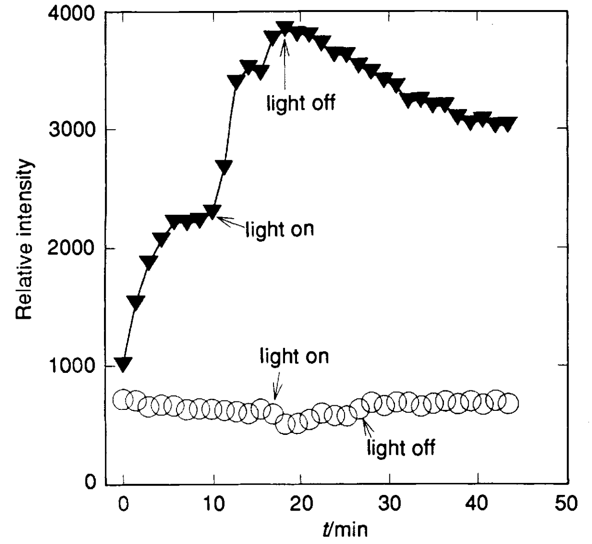

Fig. 11 Time dependence of the S–MBN• (○) and Glu–MBN• EPR signals (▼) in a solution of SCl or GluCl and MBN in dichloromethane in the dark and under illumination (unfiltered UV light)

appears to give a rather weak signal,[27] presumably due to electrophilic reactivity of the same type as demonstrated above (Figs. 3 and 4) for Cl–PBN•. It was not possible to intercept Cl–DTBE• by conducting the photolysis of GluCl–DTBE in benzene, even at 0 °C; no signals whatsoever were detectable, in spite of the fact that any chlorine adduct would be easily distinguishable.[27a] The fact that DTBE gives spin adducts of S or T by photosensitized oxidation of DTBE and S^- or T^- shows that also this spin trap can undergo inverted spin trapping, and this fact must be considered in interpreting results from photolysis experiments.

The formation of the trichloromethyl adduct must result from excitation of CCl_4 and oxidation of DTBE to $DTBE^{•+}$ by the excited state with formation of $CCl_4^{•-}$. This radical anion breaks down to Cl^- and $Cl_3C^•$ which is trapped by DTBE.

As in the case of PBN, photolysis of Im–Br (Im = S, T, Glu and P) with DTBE in dichloromethane or benzene did not give any EPR signals. However, in carbon tetrachloride SBr–DTBE during the first few min gave the signal of S–DTBE• which was then replaced slowly by the signal from Cl_3C–DTBE•, similar to the behaviour shown in Fig. 8. The same behaviour was exhibited by TBr and PBr on a somewhat longer timescale, while photolysis of GluBr–DTBE gave directly the signal of the trichloromethyl spin adduct.

The experiments conducted in carbon tetrachloride show that both ImBr and ImCl can be used to produce imidyl spin adducts from DTBE. The curious time dependence of the Im–DTBE• signals presumably depends on the low solubility of ImX in carbon tetrachloride, leading to depletion of ImX after only a short period of photolysis. Thus the steady-state concentration of Im–DTBE• cannot be sustained and the trichloromethyl adduct takes over.

Trapping of Imidyls by MBN.—This spin trap has earlier[8] been shown to give the imidyl adduct by treatment with SBr *even in the dark*. This is characterized by a 27-line spectrum with $a^N = 1.46$, $a^{H(2)} = 1.12$ and $a^{N'} = 0.14$ mT (in benzene solution).

It was first established that MBN can undergo inverted imidyl spin trapping by showing that the oxidation of a solution of MBN–Bu_4NT in dichloromethane by tris(4-bromophenyl)-aminium ion gave rise to a strong, 27-line signal of T–MBN• ($a^N = 1.51$, $a^{H(2)} = 1.16$ and $a^{N'} = 0.147$ mT); using O_2 as the oxidant gave no signal, indicating that the pathway of eqn. (10)

$$\text{MBN} + \text{T}^- \rightleftharpoons \text{T–MBN}^- \xrightarrow{\text{ox}} \text{T–MBN}^• \quad (10)$$

is not feasible. With Bu_4NS, the same reaction gave a 27-line signal with $a^N = 1.53$, $a^{H(2)} = 1.13$ and $a^{N'} = 0.153$ mT. These spin adducts were also obtained by photolysis (cut-off < 410 nm) of MBN–Bu_4NT or Bu_4NS, using 9,10-dicyanoanthracene as a sensitizer.

Repetition of the literature experiment with SBr–MBN indeed gave a medium-strong 27-line signal ($a^N = 1.51$, $a^{H(2)} = 1.14$ and $a^{N'} = 0.153$ mT) which increased in intensity on irradiation with unfiltered UV light (Fig. 10, ○). TBr–MBN showed similar behaviour: a strong signal was already present from the dark reaction ($a^N = 1.52$, $a^{H(2)} = 1.16$ and $a^{N'} = 0.143$ mT) and it increased upon irradiation with unfiltered light (Fig. 10, ▼). No effect on the dark reaction was seen by conducting the reaction in the presence of phenylacetylene. *N*-Bromophthalimide (PBr) also gave a strong signal ($a^N = 1.51$, $a^{N(2)} = 1.10$ and $a^{N'} = 0.168$ mT) arising from the dark reaction.

N-Chloroimides behaved in the same way: a strong signal of Im–MBN• developed immediately upon mixing. For GluCl–MBN, the dark signal built up to a maximum value over *ca.* 10 min, and irradiation rapidly increased the signal intensity by a factor of two. Discontinuation of the illumination led to a slow decay of the signal (see Fig. 11, ▼). In the case of SCl–MBN no increase in intensity was seen upon irradiation as shown in Fig. 11, where the reaction was monitored over 45 min with an intervening period of irradiation of 10 min. After overnight decay of S–MBN•, the remaining signal exhibited a 3 × 2 pattern ($a^N = 7.09$, $a^H = 1.33$), most likely originating from the corresponding carbonyl aminoxyl, HCON(O•)Bu^t, with a similar nitrogen coupling constant to other aminoxyls of this type.[1d]

In view of the conspicuous similarity of the EPR signals from the assumed S, T and P adducts of MBN, one might suspect that these signals are identical and originate from one and the same species, not connected to the imidyl chemistry invoked. This was however refuted by the appearance of the EPR spectrum of the glutarimidyl adduct. Its EPR spectral parameters ($a^N = 1.58$, $a^{H(2)} = 1.33$ and $a^{N'} = 0.082$; see Fig. 12) deviate significantly from those of the five-membered ring imidyl spin adducts, so there can be little doubt as to the identity of these radical species.

The fact that Glu–MBN• could be generated photochemically

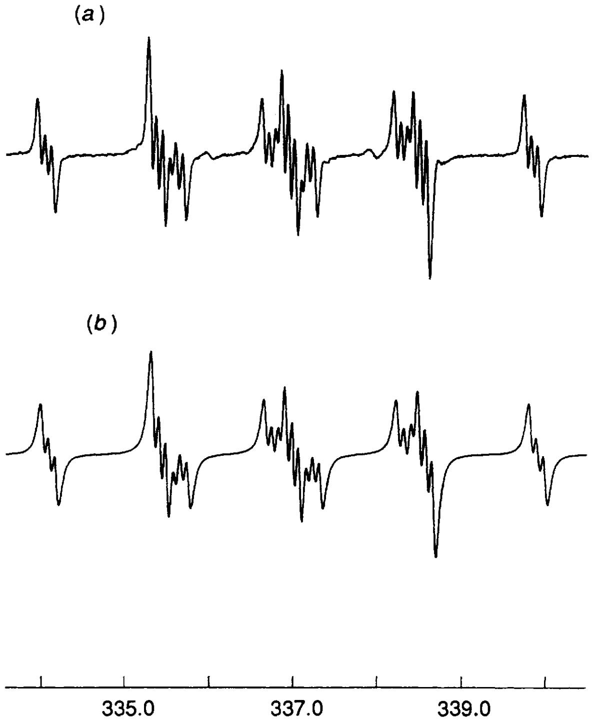

Fig. 12 (*a*) EPR spectrum of Glu–MBN$^\bullet$ obtained by irradiation (unfiltered light) of a solution of MBN and GluCl in dichloromethane; (*b*) simulated spectrum with $a^{N} = 1.58$, $a^{H(2)} = 1.33$ and $a^{N'} = 0.082$ mT; Lorentzian lineshape and linewidth = 0.12 mT

in dichloromethane was followed up by experiments in benzene to establish whether the chloro adduct might possibly be formed under these conditions (*cf.* PBN above). Photolysis of GluCl–MBN in benzene for about 5 min indeed produced a faint signal assigned to ^{37}Cl–MBN$^\bullet$ (tentatively $a^{N} = 1.20$, $a^{35Cl} = 0.68$ and $a^{H(2)} = 0.11$ mT; *cf.*[1d] those of ^{37}Cl–PBN$^\bullet$, $a^{N} = 1.21$, $a^{35Cl} = 0.605$ and $a^{H} = 0.075$ mT) together with a stronger one originating from HCON(O$^\bullet$)Bu^t ($a^{N} = 0.696$ and $a^{H} = 0.138$ mT).

MBN and MNP behave analogously in that both undergo a dark reaction with ImX (Figs. 1, 2, 10 and 11) to give Im spin adducts, although MBN is far more reactive in this respect. It is not entirely clear how this reaction should be formulated, but one possibility is that it might be caused by the presence of spurious amounts of acid in the medium, leading to an initial burst of formation of oxidative species, *e.g.*, bromine, which oxidizes the spin trap to the radical cation. The latter then reacts with ImH/Im$^-$. This idea was tested by carrying out the dark reaction in the presence of a hindered pyridine base (2,6-di-*tert*-butylpyridine), but no effect of the base was seen. The dark reaction cannot be a radical chain reaction, since the spin trap by its nature scavenges radicals and thus breaks any chain process, nor is any thermal electron transfer between ImX and MBN (MNP) likely because of the endergonicity of such a step, *ca.* 1.4 eV.

Comparative Discussion.—A glance at Table 1 shows that the task of defining mechanisms of spin trapping from ImX is very complicated indeed. Apart from the fact that spin traps (MNP, PBN, MBN) can be photo-excited to strongly reducing species which can undergo reactions of the type shown in eqn. (4) with ImX, the haloimides can also be excited and produce very reactive oxidants, apart from simple homolytic cleavage of the excited state. Thus the stage is set for a complex interplay of reactive species where it is very difficult to pinpoint any specific mechanism for formation of the spin adduct. The first lesson of this study is indeed that photoinitiated spin trapping will seldom be traceable to an unambiguous mechanism!

Yet, if we start with PBN as an anchor point, its behaviour toward ImBr under photolytic conditions rather clearly points to an inverted trapping mechanism analogous to eqn. (8), with PBN instead of MNP. In the presence of a bromine trap, Im–PBN$^\bullet$ is protected toward oxidation and is detectable. For PBN–ImCl systems, it also is clear that the opposite cleavage mode of Im–Cl$^{\bullet -}$ [eqn. (6)] manifests itself in an inverted trapping mechanism, involving initial collapse of the PBN$^{\bullet +}$ Cl$^-$ ion pair to give PBN–Cl$^\bullet$, followed by nucleophilic reaction of the latter with ImH–Im$^-$ [as exemplified for MNP in eqn. (9)]. It is then logical to extend this mechanism to the closely related MBN, the photochemical reactions of which are similar. The dark reactions of MBN–ImX still represent a bit of a puzzle, but does not detract from the approximate *photochemical* equivalence of PBN and MBN.

Although Cl–MNP$^\bullet$ was never observed from the photolysis of MNP–ImCl systems, it is still an attractive hypothesis to formulate its reactions with ImX as in eqns. (8) and (9). It is necessary to excite MNP in order to obtain the spin adducts, and given this fact, the radical cation mechanism appears to be best in accordance with the reactions described here and elsewhere.[7–9]

The fourth spin trap, DTBE, is different from the others by not being excitable by the UV light employed. It is sufficiently easily oxidized for inverted spin trapping to be feasible, and therefore its spin trapping mechanism toward imidyls is bound to remain ambiguous; it can react properly with Im$^\bullet$ formed by homolytic cleavage of ImX* or be oxidized to its radical cation by ImX* and engage in inverted spin trapping. Its chloro adduct is known (but never seen in our experiments) and would presumably react with ImH/Im$^-$ in the fashion of eqn. (9).

One conspicuous fact, analogous to the curious behaviour of Baskerville's hound,[28] is the total absence of any spin adduct that can reasonably be assigned to the ring-opened radical from S$^\bullet$, the β-isocyanatocarbonylethyl radical of eqn. (7). Three of the spin traps employed, MNP, PBN and MBN, are excellent traps for alkyl radicals.[1d,29] For DTBE one case of facile alkyl radical trapping is known[27b] (of methyl radicals generated by thermal decomposition of di-*tert*-butyl diperoxyoxalate) and the corresponding adduct was described as being unusually stable. Yet, trapping of the β-isocyanatocarbonylethyl radical has not been implicated in our study. Even when spin trapping experiments were performed with DTBE, using β-isocyanatocarbonylethyl bromide as starting material, only the succinimidyl spin adduct was detectable.[9] However, it should be noted that generation of the 2,2-dimethylsuccinimidyl radical led to the ring-opened radical OCNCOCH$_2$CH$_2$C(CH$_3$)$_2$$^\bullet$ which was trapped by MNP.[9] We find this apparent unreactivity of the β-isocyanatocarbonylethyl radical curious and are devising new schemes to approach this problem.

Experimental

Materials.—Except for chemicals already described in ref. 3, the following materials were either purchased or synthesized: 2-methyl-2-nitrosopropane (MNP, Aldrich), 1,1-di-*tert*-butylethylene (DTBE),[30] *N*-methylene-*tert*-butylamine *N*-oxide (MBN),[8] *N*-bromosuccinimide (SBr, Kebo, recrystallized from dichloromethane), *N*-chlorosuccinimide (SCl, Kebo, recrystallized from dichloromethane), *N*-bromotetramethylsuccinimide (TBr),[31] *N*-bromoglutarimide (GluBr),[32] *N*-chloroglutarimide (GluCl),[9] *N*-bromophthalimide (Riedel-deHaën), *tert*-butyl hypochlorite (Tokyo Kasei), 2,4,6-trianisylpyrylium (TAP) tetrafluoroborate (gift from Professor Eberhard Steckhan, Bonn University),[18] 9,10-dicyanoanthracene (Tokyo Kasei), phenylacetylene (Janssen Chimica) and cyclohexene (Kebo).

Procedures.—Spin trapping experiments were generally performed on 0.05–0.2 mol dm^{-3} solutions of the spin trap (with exception of DTBE, for which a higher concentration,[9] *ca.* 0.5 mol dm^{-3}, was used), together with 0.1–0.2 mol dm^{-3} of [ImX] (not always possible in solvents like benzene or tetrachloromethane; in such cases, saturated solutions of ImX were used) and a similar concentration of additive, if required. EPR spectra were recorded on solutions in quartz tubes of inner diameter 0.8 mm. Lateral diffusion was negligible under the time periods employed. The UV light source was the 50 W high-pressure Hg lamp from Bruker (ER 202), in appropriate cases equipped with cut-off filters from Schott, Germany. Photolyses were performed in the photolysis cavity of the Upgrade Version ESP 3220-200SH of the Bruker ER-200D spectrometer. Cyclic voltammetry was conducted for samples in acetonitrile–tetrabutylammonium hexafluorophosphate (0.2 mol dm^{-3}) with the BAS-100 instrument. UV spectra were recorded for solutions in acetonitrile or dichloromethane (HP-8452A spectrophotometer).

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