

Spin Adducts from the Reaction Between *N*-Phenyl- α -*tert*-butylnitron (PBN) and Activated Olefins. A Facile Pathway Converting PBN into 2-Methyl-2-nitrosopropane (MNP)

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N-Phenyl- α -*tert*-butylnitron (PBN) reacts with activated olefins RCH=CHR, such as maleimides, maleic anhydride or diethyl maleate, with formation of two types of persistent spin adducts giving characteristic EPR spectra, denoted types A and B. Spin adducts with type A spectrum were formed photochemically and identified as reductive coupling products between the olefin and PBN, RCH₂CH(R)–PBN'. Spin adducts with type B spectra were formed photochemically and/or thermally and were identified as reductive coupling products RCH₂CH(R)–N(O')Bu' between the olefin and a degradation product of PBN, 2-methyl-2-nitrosopropane (MNP, *t*-BuNO).

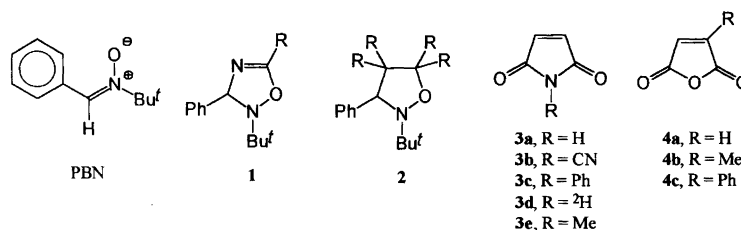
The conversion of PBN to *t*-BuNO was studied for a compound with an exceedingly reactive nitrogen-nitrogen double-bond, namely 4-phenyl-4*H*-1,2,4-triazoline-3,5-dione (PTAD). In this case, a 74% yield of *t*-BuNO was obtained in a short period of time; α ,*N*-diphenylnitron reacted similarly to give nitrosobenzene. The reaction between PBN and an activated olefin was assumed to occur analogously, either via the initial formation of a 1,3-dipolar cycloadduct or some parallel reaction involving attack of the electrophilic olefin at the PBN α -carbon. The 1,3-dipolar cycloadduct between PBN and *N*-phenylmaleimide exhibited favourable initiator properties for living polymerization of styrene.

A new type of spin adduct, RCH(Bu')CH(R)–N(O')Bu', was prepared by the photochemical reaction between an activated olefin and *t*-BuNO. This reaction presumably proceeds by photocleavage of *t*-BuNO to NO and *t*-Bu', the latter reacting with the activated olefin to give a transient radical, RCH(Bu')CH'(R), which is trapped by *t*-BuNO.

N-Phenyl- α -*tert*-butylnitron (PBN), an often used spin trap,¹ was recently shown to undergo 1,3-dipolar cycloaddition to activated nitriles with formation of isoxadiazolidines **1**² or to olefins with formation of isoxazolines **2**.³ Such reactions must be kept under control in order not to interfere with the use of PBN as a spin trap.

In a recent study⁴ it was found that certain cyclic

activated olefins reacted photochemically with PBN to form a mixture of aminoxyls which gave rise to a superposition of two characteristic EPR spectra. The behaviour of maleimide (**3a**) was typical. It gave a mixture of a major 3 × 2 × 2-line spectrum, a^N 1.44, $a^{\alpha-H}$ 0.68 and $a^{H'}$ 0.060 mT, and a minor spectrum of higher complexity (ca. 40% in relation to the other spectrum),



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featuring two nitrogen couplings and four hydrogen couplings, each of multiplicity 1 (a^N 1.44, $a^{N'}$ 0.060, a^H 0.116, $a^{H'}$ 0.099, $a^{H''}$ 0.079 mT and $a^{H'''} 0.059$ mT). These spectra will be denoted type A and type B, respectively, in the following (Fig. 1a).

Spectrum A of Fig. 1a changed in the way expected for a PBN spin adduct when PBN- α -(^2H) was used, in that the large α -H coupling of 0.68 mT was replaced by an estimated α -(^2H) coupling of 0.105 mT. This indicates that spectrum A should correspond to a spin adduct of PBN. The A spectrum now became hidden below the B spectrum which on the other hand was unchanged by the switch from PBN to PBN- α -(^2H) (Fig. 1b). Thus spectrum B cannot correspond to a spin adduct of PBN but must have a more complicated origin. Similar superpositions of types A and B spectra were observed by the photolysis of PBN and *N*-cyanomaleimide (**3b**), *N*-phenylmaleimide (**3c**) or maleic anhydride (**4a**).

The A type spectrum in Fig. 1a could also be detected from the photolysis of succinimide (**5**), PBN and di-*tert*-butyl peroxide in dichloromethane. In these reactions, it is assumed from previous analogies⁵ that a hydrogen atom is abstracted from an α -position of succinimide by a *tert*-butoxyl radical giving a 3-succinimidyl radical (**6**) which is trapped by PBN. A weak EPR spectrum with a^N 1.44 and $a^{\alpha\text{-H}}$ 0.66 mT was detected; the broad lines ($\Delta H_{\text{pp}}=0.107$ mT) indicated further coupling. It was not possible to detect any contribution from the B type spectrum since it would be totally obscured by the spectrum of *t*-BuO-PBN \cdot , inevitably formed as the major aminoxyl component by trapping of *t*-BuO \cdot . On this basis, the A type spectrum from maleimide was assigned to the spin adduct **7a**, formally derived from PBN by trapping of the 3-succinimidyl radical **6**. Viewing the mechanism of formation of **7a** in a formal context, it would be classified as a reductive coupling of PBN and maleimide.⁶

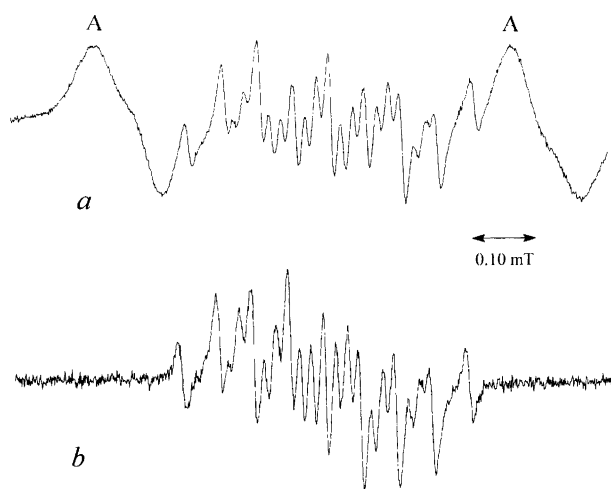
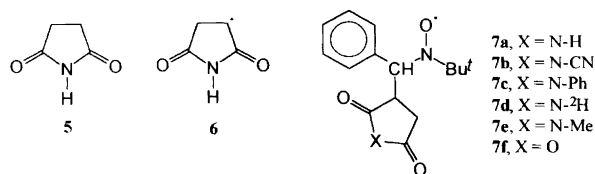


Fig. 1. The middle group of lines of the EPR spectrum recorded after daylight exposure for 10 h of a dichloromethane solution of maleimide **3a** (0.3 mol dm^{-3}) and (a) PBN (0.2 mol dm^{-3}) or (b) PBN- α -(^2H) (0.2 mol dm^{-3}).



We now report results of an extended study of this reaction, including data pertaining to the problem of the mechanism of formation of these adducts. The B type spectra are in all probability due to spin adducts of *t*-BuNO, the latter being formed by degradation of PBN. Additionally, a new type of adducts from activated olefins is described.

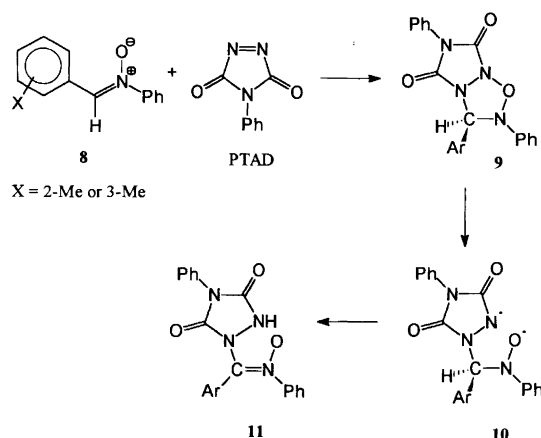
Results and discussion

General. Initially, the reactions between PBN and compounds with activated double bonds were performed by irradiation of the samples by UV light in the cavity of the EPR spectrometer or external irradiation by a 300 W 'sun lamp'. However, the EPR spectra thus observed were not always well resolved, especially those of the B type. Later, it was discovered that exposure to diffuse daylight in many cases produced intense, well resolved EPR spectra which lasted for long periods. Unless otherwise stated, daylight exposure was the method preferred for promoting the reactions. Since the critical reactions were dependent on second-order kinetics, the concentrations of the reactants were kept at $0.2\text{--}0.3 \text{ mol dm}^{-3}$ in order to achieve convenient reaction rates.

In their reactions with PBN, compounds with activated double bonds were characterized according to the redox potential at which they undergo one-electron reduction: the more easily reduction occurs, the more reactive the compound is toward PBN. In the most reactive cases, even thermal reactions were observed. Below, we will describe the various reactions in approximately descending reactivity order. The possible mechanisms will be discussed as the mechanistic problems appear in order to build up a consistent picture of the reactions leading to aminoxyls with EPR spectra of type A and B.

The reaction between PBN and 4-phenyl-4H-1,2,4-triazoline-3,5-dione (PTAD). PTAD, with $E^\circ(\text{PTAD}/\text{PTAD}^{\cdot-})=0.07 \text{ V vs. SCE}$, is one of the most reactive dienophiles and dipolarophiles known.⁷ It has been suggested to react with α -(2-methyl- or 3-methyl-phenyl)-*N*-phenylnitrene (**8**) in benzene at 20°C according to Scheme 1 below.⁸ It was claimed that the initial product formed was the cycloadduct **9** which underwent homolytic cleavage to give diradical **10**. Hydrogen atom migration in the latter would give nitrene **11** which was assumed to be the final product.⁸

Upon dissolving a slight deficit of PTAD (70 mmol dm^{-3}) in a solution of PBN (80 mmol dm^{-3}) in dichloromethane the red colour of PTAD changed to



Scheme 1.

green within 2 min. The EPR spectrum of the green solution consisted of two weak 1:1:1 triplets, one belonging to $t\text{-Bu}_2\text{NO}^\cdot$ ($a^N = 1.58 \text{ mT}$, lit.⁹ 1.584 mT) and the other to $\text{PhCON}(\text{O}^\cdot)\text{Bu}^t$ ($a^N = 0.805 \text{ mT}$, lit.⁹ 0.80 mT). Irradiation by filtered light of $\lambda > 400 \text{ nm}$ produced an intense signal of two overlapping spectra with broad lines ($\Delta H_{\text{pp}} \approx 0.07 \text{ mT}$), one corresponding to $t\text{-Bu}_2\text{NO}^\cdot$ (ca. 5%) and the second one (95%) exhibiting couplings to three different nitrogens, $a^N = 0.140, 0.610$ and 0.741 mT . There were also indications of a third, weaker spectrum, but it was almost completely obscured by the two other spectra. The signal remained for hours after discontinuation of irradiation. After 20 h, a strong signal due to $t\text{-Bu}_2\text{NO}^\cdot$ remained.

In another experiment, a deficit of PBN (40 mmol dm^{-3}) was added to a solution of PTAD (90 mmol dm^{-3}). The red colour of PTAD remained, and the solution, 2 min after mixing, displayed the composite EPR spectrum shown in Fig. 2a. Irradiation of

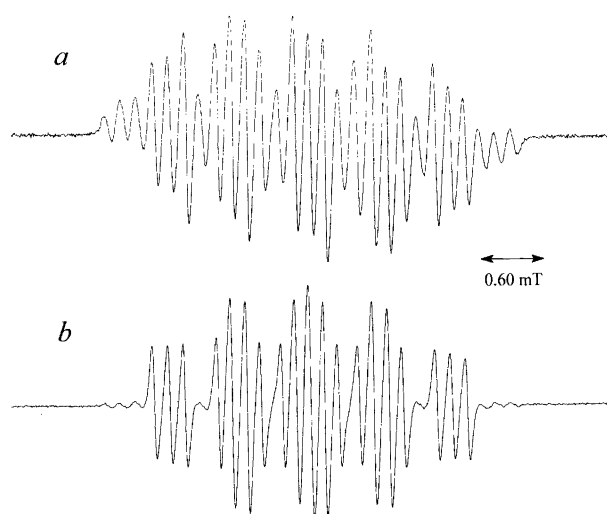


Fig. 2. EPR spectrum recorded after mixing a solution of PTAD ($0.090 \text{ mol dm}^{-3}$) and PBN ($0.040 \text{ mol dm}^{-3}$) in dichloromethane after (a) mixing under dark conditions and (b) irradiation for 5 min by light of $\lambda > 400 \text{ nm}$.

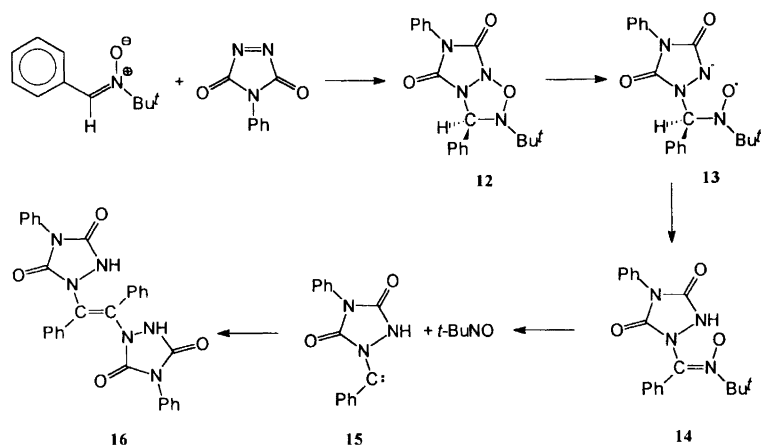
this solution by light of $\lambda > 400 \text{ nm}$ rapidly amplified part of the spectrum (Fig. 2b), the EPR parameters of which ($a^N = 0.147, 0.615$ and 0.759 mT) were almost the same as those found above. The second, weaker spectrum could not be analyzed, since most of it was obscured by the other spectrum. The same superposition of spectra and behaviour on irradiation was observed in experiments carried out with PBN- $\alpha(^2\text{H})$ as the substrate or with ($^2\text{H}_2$)dichloromethane as the solvent.

^1H NMR spectral monitoring of the green solution formed by the reaction between PBN (22 mmol dm^{-3}) and PTAD (20 mmol dm^{-3}) in (^2H)chloroform showed that the easily recognizable peak from the $\alpha\text{-H}$ of PBN disappeared within 5 min, and that the resulting solution had an NMR spectrum with no significant characteristics, except for the fact that a peak at $\delta 1.27 \text{ ppm}$ indicated that $t\text{-BuNO}$ had been formed in 74% yield. No indication of the presence of the cycloadduct between PTAD and PBN was seen. A preparative experiment led to the detection of a 70% yield of a water-sensitive dimeric product, the structure of which was assumed to be **16** (see Experimental and discussion below). UV spectral monitoring of the reaction between PTAD and PBN at 544 nm gave a rate constant of $2.8(1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 23°C , unchanged when PBN- $\alpha(^2\text{H})$ was used as the substrate. The formation of $t\text{-BuNO}$ was shown by the appearance of its weak absorption band at $\lambda_{\text{max}} = 678 \text{ nm}$.

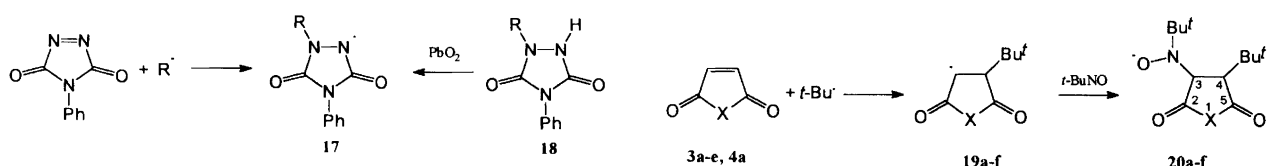
A similar reaction between PTAD and α,N -diphenyl-nitron gave the same dimer **16** in a reaction which was essentially over after mixing. The yield of nitrosobenzene was 78%, as determined by UV spectroscopic analysis.

Previous findings⁸ and the results described above suggest that Scheme 2 below includes the most important steps of the PBN-PTAD reaction. By analogy with Scheme 1, the cycloadduct **12** is first formed but decomposes rapidly in the same way as shown for **9**, giving the substituted urazole derivative **14**. Loss of $t\text{-BuNO}$ (formed in 74% yield) from **14** gives carbene **15** which dimerizes to the alkene **16**. No experiments to trap **15** by added olefins were attempted. The further purification of **16** was thwarted by its high sensitivity to traces of water, the final products being benzaldehyde and 4-phenylurazole.

PTAD is known to act as an efficient spin trap toward radicals R^\cdot , and then forms persistent urazoly radicals of type **17** shown in Scheme 3.¹⁰ One of the characteristic properties of $t\text{-BuNO}$ is its high photochemical reactivity,¹ being converted into $t\text{-butyl}$ radical and NO . If no other reactant is available, $t\text{-Bu}^\cdot$ will add to $t\text{-BuNO}$ (rate constant $3 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in benzene),¹¹ giving the extremely persistent $t\text{-Bu}_2\text{NO}^\cdot$, whereas in the presence of a more reactive substrate $t\text{-Bu}^\cdot$ should add to the latter. Thus the major radical species detected by EPR spectroscopy is assigned as the $t\text{-butylurazoly}$ radical **17**, $\text{R} = t\text{-Bu}$, formed by addition of $t\text{-Bu}^\cdot$ to PTAD (Scheme 3). This radical has been prepared by oxidation of authentic 1-*tert*-butylurazole (**18**, $\text{R} = t\text{-Bu}$)



Scheme 2.



Scheme 3.

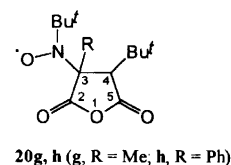
and showed $a^N = 0.145$, 0.605 and 0.750 mT in benzene solution.¹² These parameters are nearly the same as those given above for the major radical of Fig. 2. A similar radical [17, $R = \text{Ph}(\text{CH}_3)_2\text{C}^\cdot$], prepared by trapping of the cumyl radical by PTAD, had $a^N = 0.146$, 0.633 and 0.775 mT in cumene.¹⁰

The conclusion that the photochemical reaction of $t\text{-BuNO}$ and PTAD is responsible for the radicals formed in the rapid thermal reaction between PBN and PTAD was verified by mixing solutions of $t\text{-BuNO}$ in the concentration range of $1\text{--}120$ mmol dm^{-3} with PTAD and recording the EPR spectra of the resulting solutions after exposure to light. Mixtures of EPR spectra of identical appearance as that shown in Fig. 2a were obtained.

Thus, with the exceedingly reactive dipolarophile PTAD the reaction with PBN rapidly leads to the establishment of a significant concentration of $t\text{-BuNO}$ in a thermal reaction with the PTAD-PBN cycloadduct 12 as a postulated but transient intermediate. The radicals detected were derived from the photochemical cleavage of $t\text{-BuNO}$. This finding suggests that $t\text{-BuNO}$ might also be formed in the reactions of PBN with other, less reactive dipolarophiles, and possibly provide the origin of the B type spectra. For example, it may be that the cycloadduct between PBN and the olefin is formed slowly and decomposes with formation of $t\text{-BuNO}$, analogously to the sequence outlined in Scheme 2. Photolytic decomposition of $t\text{-BuNO}$ might then lead to addition of $t\text{-Bu}^\cdot$ to the olefin, as shown in Scheme 4. The resulting radical 19 should be a reactive one, capable of adding to $t\text{-BuNO}$ with formation of a persistent spin adduct (20).

Below, the results from testing this hypothesis are described. While the expected radicals 20 were easily

Scheme 4.



- a, X = N-H
- b, X = N-CN
- c, X = N-Ph
- d, X = N-2H
- e, X = N-Me
- f, X = O

prepared and characterized by EPR spectroscopy, none of them displayed EPR spectra denoted as type B.

The reaction between $t\text{-BuNO}$ and activated olefins. A solution of $t\text{-BuNO}$ ($1\text{--}100$ mmol dm^{-3}) and an activated olefin (0.2 mol dm^{-3}), like N -phenylmaleimide, in dichloromethane immediately after mixing (exposure to laboratory light conditions for 2 min) showed very low paramagnetic activity. Exposure to daylight for 2–3 min produced a persistent radical with a well resolved EPR spectrum (Fig. 3a), a^N 1.44 (1 N), a^{H^3} 0.160 (1 H), a^{H^4} 0.094 (1 H), $a^{t\text{-Bu}}$ 0.019 (9 H) and a^{N^1} 0.094 (1 N) mT. Further light exposure for 15 min enhanced the intensity of the spectrum strongly, but at the expense of the resolution (Fig. 3b).

The EPR spectral parameters of this radical are in good agreement of those expected for a spin adduct of $t\text{-BuNO}$ in which a radical of the general structure $\text{X}_2\text{CH}_A^\cdot$ has been attached to the nitrogen atom. Such a radical should have $a^N \sim 1.45$ mT and a^{H^A} in the range $0.1\text{--}0.2$ mT.^{1b} As is common for $t\text{-BuNO}$ spin adducts, couplings to atoms in the trapped radical are resolved.

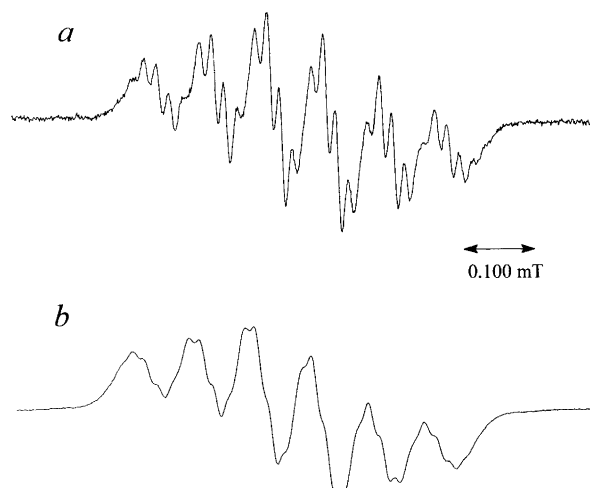


Fig. 3. The middle group of lines of the EPR spectrum recorded from a solution of *t*-BuNO (0.050 mol dm⁻³) and *N*-phenylmaleimide **3c** (0.3 mol dm⁻³) in dichloromethane after daylight exposure for (a) 3 and (b) 18 min.

We thus assign structure **20c** to this radical, formed according to the reactions shown in Scheme 4.

A series of cyclic derivatives of maleic acid was then allowed to react with *t*-BuNO in a similar way. Similar spin adducts were obtained in all cases but one, where only *t*-Bu₂NO[•] was detected. This was dimethylmaleic anhydride, for which the addition of *t*-Bu[•] to the double bond presumably is too slow to compete with addition to *t*-BuNO. The EPR parameters are given in Table 1. The spectra are assigned to structures **20**, in the appropriate cases guided by the assumption that the initial attack of *t*-Bu[•] will occur at the less hindered position. The response of *a*^N to introducing one substituent in maleic anhydride (methyl- and phenyl-) was the expected one for going from an X₂CH to an X₃C radical (see **20g, h**), namely to increase from ~1.45 to ~1.60 mT.^{1b}

Also noncyclic activated olefins **21** underwent photochemical reaction with *t*-BuNO in dichloromethane, as detected by EPR spectroscopy. The EPR spectral parameters are given in Table 2, and the spectra are assigned

to radicals **22**, formed from **21** in the same way as shown in Scheme 4 and with the same assumption that *t*-Bu[•] attacks at the least hindered position. Recently,¹³ the same structure (**22d**) was assigned to the radical formed upon dissolution of *t*-BuNO in neat diethyl fumarate. In this case, two diastereomers with slightly differing EPR spectral properties (Table 2) were characterized, but only the two largest coupling constants were detected. In some cases (the last five compounds of Table 2), no radical of structure **22** was detectable. Instead, strong signals from *t*-Bu₂NO[•] were seen. This behaviour must reflect competition between addition of *t*-Bu[•] to *t*-BuNO ($k = 3 \times 10^6$ dm³ mol⁻¹ s⁻¹) and the relevant olefin. Rate constants for the latter reaction are known for a number of olefins,¹⁴ but unfortunately not for activated ones of the type giving adducts **20** or **22**. The most reactive olefin studied, 2-vinylpyridine, reacted with *t*-Bu[•] with $k = 4.6 \times 10^5$ dm³ mol⁻¹ s⁻¹, not rapid enough to compete with *t*-BuNO (Table 2).



- a (R¹=H, R²=H, R³=COOMe)
- b (R¹=H, R²=CH₃, R³=COOMe)
- c (R¹=COOEt, R²=H, R³=COOEt; *cis*)
- d (R¹=COOEt, R²=COOEt, R³=H; *trans*)
- e (R¹=COOMe, R²=COOMe, R³=H; *trans*)
- f (R¹=H, R²=H, R³=CN)
- g (R¹=H, R²=CH₃, R³=CN)
- h (R¹=CN, R²=H, R³=CN; *trans*)

It was also shown that the rate constants for the reactions between *t*-Bu[•] and monosubstituted and 1,1-disubstituted olefins increased with increasing gas-phase electron affinity (*EA*) according to

$$\log(k_{300}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 6.0 + 1.6 \times EA$$

thus classifying *t*-Bu[•] as a nucleophilic species. Even if this correlation cannot be applied strictly to 1,2-disubstituted olefins **3**, **4a** and **21h** (the electron affinities of maleate and fumarate esters **21c–e** are not known, but

Table 1. Spin adducts of type **20** from solutions of cyclic activated olefins **3** and **4** (0.2 mol dm⁻³) and *t*-BuNO (0.050 mol dm⁻³) in dichloromethane, exposed to diffuse daylight for 0.03–20 h.^a

Activated olefin, 3	<i>EA</i> of 3 / eV ^b	<i>a</i> ^N /mT	<i>a</i> ^{H3} /mT	<i>a</i> ^{H4} /mT	<i>a</i> ^{H(t-Bu)} / mT	<i>a</i> ^{N'} /mT	<i>a</i> ^{H-N} /mT	Assigned to structure
Maleimide (3a)	1.16	1.45	0.175	0.079	0.020 (9)	0.080	0.090	20a
<i>N</i> -(² H)Maleimide (3d)	1.16	1.45	0.175	0.079	0.020 (9)	0.080	0.014 (D)	20d
<i>N</i> -Phenylmaleimide (3c)	1.36	1.44	0.160	0.080	0.019 (9)	0.081	—	20c
<i>N</i> -Cyanomaleimide (3b)	—	1.42	0.154	0.076	0.016 (9)	0.108	—	20b
<i>N</i> -Methylmaleimide (3e)	1.12	1.44	0.182	0.084	0.016 (9)	0.087	—	20e
Maleic anhydride (4a)	1.44	1.44	0.154	0.085	0.015 (9)	—	—	20f
Methylmaleic anhydride (4b)	1.29	1.59	0.066 (3) ^c	0.103	0.033 (9)	—	—	20g
Dimethylmaleic anhydride	1.16	No reaction		—	—	—	—	—
Phenylmaleic anhydride (4c)	1.78	1.60	0.130 ^d	0.080	0.033 (9)	—	—	20h

^aThe multiplicity of each coupling was 1, unless otherwise stated (number in parentheses). ^bTaken from Refs. 14 and 33.

^cCoupling to hydrogens of the 3-methyl group. ^dCoupling to 4-hydrogen of the 3-phenyl group.

Table 2. Spin adducts of type **22** from solutions of acyclic activated olefins **21** and a few other compounds with activated double bonds ($0.2\text{--}0.5\text{ mol dm}^{-3}$) and $t\text{-BuNO}$ (0.050 mol dm^{-3}) in dichloromethane, exposed to diffuse daylight for $0.03\text{--}20\text{ h}$.^a

Activated olefin, 21	EA of 21 / eV ^b	a^N/mT	a^{H1}/mT	a^{H2}/mT	$a^{H(t\text{-Bu})}/\text{mT}$	$a^{\text{other}}/\text{mT}$	$a^{N'}/\text{mT}$	Assigned to structure
Methyl acrylate (21a)	-0.49	1.45	0.258	0.060 (2)	—	0.022 (3)	—	22a
Methyl methacrylate (21b)	-0.38	1.57	—	0.080 (2)	—	0.028 (3) ^c	—	22b
Diethyl maleate (21c)	—	1.45	0.266	0.062	—	0.024 (4)	—	22c
Diethyl fumarate (21d)	—	1.45	0.269 ^d	0.059	—	0.024 (4)	—	22d
Dimethyl fumarate (21e)	—	1.46	0.276	0.066	—	0.023 (6)	—	22e
Acrylonitrile (21f)	-0.21	1.51	0.147	0.053 (2)	—	—	0.025	22f
2-Methylacrylonitrile (21g)	-0.17	1.57	—	0.084 (2)	—	0.040 (3)	—	22g
Fumaronitrile (21h)	1.24	1.51	0.221	0.025	—	—	0.043	22h
Diethyl acetylenedicarboxylate	—	1.57	—	—	—	—	—	$t\text{-Bu}_2\text{NO}^\cdot$
Diethyl azodicarboxylate	—	1.58	—	—	—	—	—	$t\text{-Bu}_2\text{NO}^\cdot$
2-Vinylpyridine	-0.41	1.58	—	—	—	—	—	$t\text{-Bu}_2\text{NO}^\cdot$
4-Vinylpyridine	—	1.57	—	—	—	—	—	$t\text{-Bu}_2\text{NO}^\cdot$
Azobenzene	0.57	1.58	—	—	—	—	—	$t\text{-Bu}_2\text{NO}^\cdot$

^aThe multiplicity of each coupling was 1, unless otherwise stated (number in parentheses). ^bTaken from Refs. 14 and 33. ^cCoupling to 2-CH_3 or ester CH_3 . ^dLit.:³⁴ a^N 1.42 (1.465), a^{H2} 0.28 (0.235) in neat diethyl fumarate for what were assumed to be two diastereomers; no further couplings were reported.

are likely to be similar to that of **21h**) or trisubstituted olefins **4b** and **4c**, their large electron affinities indicate that the addition rate constants should be of the order of $10^8\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ or higher, well above that of addition of $t\text{-Bu}^\cdot$ to $t\text{-BuNO}$.

Finally, it should once more be stressed that the EPR spectra of Tables 1 and 2 in no case corresponded to the type B spectra obtained from PBN and activated olefins.

The reaction between PBN and N-phenylmaleimide 3c. According to its electron affinity and redox potential (Tables 1 and 3), *N*-phenylmaleimide should be the most reactive of the olefins studied, and was therefore chosen for a more detailed study of its reaction with PBN. Moreover, the B spectrum resulting from this reaction was the best resolved one, making any changes in the spectral composition easy to follow. Thirdly, the cycloadduct between **3c** and PBN (**23c**, see below) was easily accessible for separate study.

A solution of PBN (0.18 mmol dm^{-3}) and *N*-phenylmaleimide (0.18 mmol dm^{-3}) was split into two parts and put into two EPR tubes. One tube was exposed to daylight, whereas the other one was kept in the dark. EPR spectra were then monitored at regular intervals for a period of 20 days.

In the tube exposed to daylight, a two-component EPR spectrum developed slowly. It was clearly discernible after 2 h, well developed and resolved after 12 h, and both spectra kept growing during 100–150 h of irradiation to a constant concentration level (Fig. 4) which remained for at least 50–100 h. According to the previous classification (Fig. 1), the spectrum consisted of one component A (ca. 70%) with $a^N = 1.44\text{ mT}$, an unusually large $a^{\alpha\text{-H}}$ of 0.626 mT , and $a^{H'} = 0.060\text{ mT}$, and a second component B with a more complex spectrum, $a^N = 1.458\text{ mT}$, $a^{N'} = 0.063$, $a^{H'} = 0.077$, $a^{H''} = 0.094$ and $a^{H'''} = 0.116\text{ mT}$. The middle group of lines of spectra A + B is shown in Fig. 5a, together with a simulation with the parameters given (Fig. 5b). An identical spectrum was obtained when ($^2\text{H}_2$)dichloromethane was the solvent. A slightly different spectrum was obtained in acetonitrile (Table 3) where the reaction proceeded more slowly.

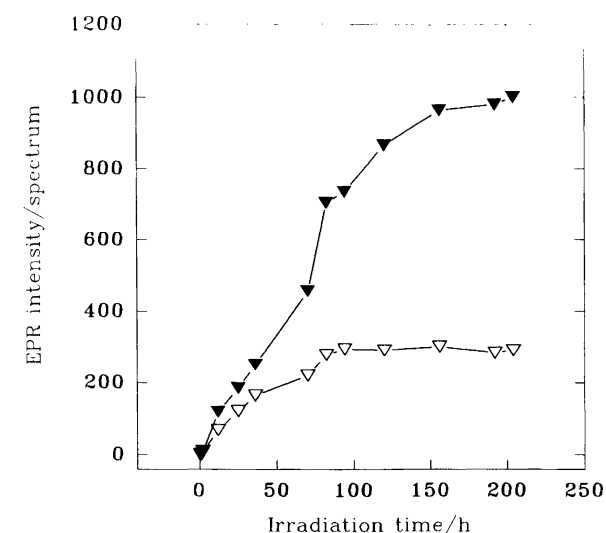


Fig. 4. EPR spectral intensity recorded from a solution of PBN (0.18 mol dm^{-3}) and *N*-phenylmaleimide **3c** (0.18 mol dm^{-3}) in dichloromethane as a function of time of daylight exposure. Empty triangles: spectrum A. Filled triangles: spectrum B.

With PBN- $\alpha(^2\text{H})$, a similar reaction produced an EPR spectrum where the large coupling constant of spectrum A had been eliminated and accordingly spectrum A had become hidden under spectrum B (Fig. 5c). The latter was unchanged by the isotopic substitution, as also was found for the type B spectrum from maleimide and PBN.

The sample of PBN-*N*-phenylmaleimide kept in the

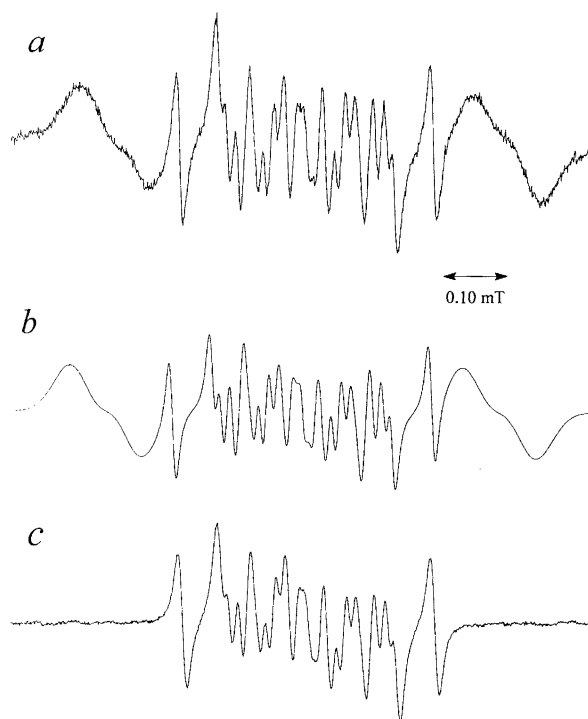


Fig. 5. (a) The middle group of lines of the EPR spectrum recorded from a solution of *N*-phenylmaleimide **3c** (0.18 mol dm^{-3}) and PBN (0.18 mol dm^{-3}) in dichloromethane, irradiated for 10–250 h by diffuse daylight. (b) Simulated spectrum, using the parameters given in Table 1 and a linewidth of 0.035 (A) or 0.010 (B) mT. (c) The middle group of lines of the EPR spectrum recorded from a solution of *N*-phenylmaleimide **3c** (0.2 mol dm^{-3}) and PBN- $\alpha(^2\text{H})$ (0.2 mol dm^{-3}) in dichloromethane, irradiated for 20 h by diffuse daylight.

dark also slowly developed a weak but well resolved EPR spectrum consisting only of the B component. The signal grew slowly over ca. 80 h under dark conditions, after which time the solution was exposed to daylight conditions. The B spectrum then rapidly increased, and the A spectrum started to develop. Thus the radical responsible for the A spectrum is only formed under photochemical conditions, while the species corresponding to the B spectrum is generated both thermally and photochemically.

The addition of a low concentration of a source of deuterons, $(^2\text{H}_2)\text{SO}_4$ (25 mmol dm^{-3}) initially had no effect of either the A or B spectrum from PBN and *N*-phenylmaleimide, except that the development of the EPR spectrum was slower. However, after some 40–50 h of exposure to daylight, the original B spectrum had decreased in intensity and been displaced by a spectrum which was best described by having the two hydrogens with $a^{\text{H}''} = 0.094$ and $a^{\text{H}'''} = 0.116 \text{ mT}$ partially replaced by deuteriums.

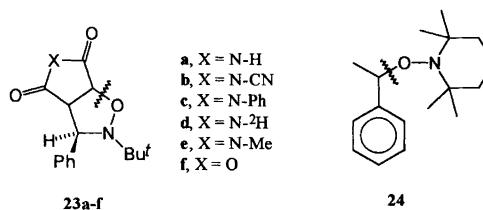
With a base (3,5-lutidine) present, spectra A+B appeared but at a slower rate.

Since it was assumed above that *t*-BuNO is somehow formed in solutions of PBN and *N*-phenylmaleimide, as

in the PTAD–PBN reaction, it remains to provide a credible explanation why the EPR spectrum of **20c** was not seen under the conditions of the experiment shown in Fig. 4. Therefore, after discontinuation of this experiment, the solution was made 0.7 mM in *t*-BuNO, and the sample monitored for a second irradiation period of ca. 80 h. The results are shown in Fig. 6. Upon addition of *t*-BuNO (at arrow), the intensity of the A spectrum immediately went down by about 10%, caused by dilution, and then remained almost constant over 80 h. By contrast, the intensity of the B spectrum went down by a factor of 4–5 over 12 h and then slowly increased again during the next 80 h. The accompanying changes in the A+B spectrum were small, as seen from Fig. 7, showing the A+B spectrum before the addition of *t*-BuNO (Fig. 7a), the maximally changed spectrum during the transition period (Fig. 7b) and the final spectrum after 80 h (Fig. 7c). The spectrum of Fig. 7d shows a simulation of the B spectrum from *N*-phenylmaleimide, superimposed upon the spectrum of **20c** in a ratio of 1:1. It is obvious that the presence of the spectrum of **20c** does not perturb the B spectrum very much, and therefore a low proportion of **20c** would be difficult to detect.

Thus, under conditions where *t*-BuNO and *N*-phenylmaleimide alone would have given a strong spectrum of **20c**, no clear indication of this spectrum was obtained when the species corresponding to the B spectrum was present. Evidently, a mechanism for the consumption of **20c** must exist under these conditions (see below).

Synthesis and properties of the cycloadduct between PBN and N-phenylmaleimide. By analogy with α,N -diarylnitrones,¹⁵ PBN reacted slowly with *N*-phenylmaleimide (EtOH, reflux, 72 h) and gave the cycloadduct **23c** in 70% yield. After recrystallization from dichloromethane–hexane, the sample displayed an EPR spectrum identical to component B of Fig. 4a. Heating it to 40°C in dichloromethane solution did not affect the concentration of the radical, whereas heating to 100°C in *p*-xylene eliminated the EPR spectral signal. Irradiation did not affect the concentration of the radical. Treatment with a nucleophile (hydrogendiacetate ion) destroyed the radical. ^1H NMR spectral examination of the sample revealed an impurity at the 1% level with the expected characteristics of the three-spin system of the 3,4-hydrogens of a succinimide substituted by an *N*-connected group in the 3-position (see Experimental).



By virtue of its aminoxy functionality, cycloadduct **23c** is a compound similar to those employed (for an example,

Table 3. Spin adducts from solutions of activated olefins (0.2–0.3 mol dm⁻³) and PBN (0.2–0.3 mol dm⁻³) in dichloromethane, exposed to diffuse daylight for 2–100 h.^a

Activated olefin (AO)	$E(\text{AO}^{\cdot-}/\text{AO})/V$ vs. SCE	Spectrum	$a^{\text{N}}/$ mT	$a^{\alpha\text{-H}}/$ mT	$a^{\text{N}}/$ mT	$a^{\text{H}}/$ mT	$a^{\text{H}}/$ mT	$a^{\text{H}''}/$ mT	$a^{\text{H}''''}/$ mT	Assigned to
Maleimide (3a)	-0.69 ^b	A	1.45	0.68 ^c		0.070				7a
		B	1.47	—	0.060	0.059	0.079	0.099	0.116	28a
<i>N</i> -(² H)Maleimide (3d)		A	1.45	0.68 ^c		0.070				7d
		B	1.47	—	0.060	0.059	0.012 (D)	0.099	0.116	28d
<i>N</i> -Phenylmaleimide (3c)	-0.52 ^b	A	1.44	0.626 ^c		0.060				7c
		B	1.458	—	0.063	0.077	0.094	0.116		28c
<i>N</i> -Phenylmaleimide in acetonitrile		A	1.44	0.625 ^c		0.060				7c
		B	1.46	—	0.057	0.079	0.096	0.111		28c
<i>N</i> -Cyanomaleimide (3b)	-0.64 ^d	A	1.456	0.772 ^c		0.072				7b
		B	1.438	—	0.090	0.028	0.272			28b
<i>N</i> -Methylmaleimide (3e)	-0.64 ^{b,e}	A	1.43	0.66 ^c		0.055				7e
		B	1.40	—	0.112	0.02	0.03	0.23		28e
Maleic anhydride (4a)	-0.50 ^f	A	1.46	0.809 ^c		0.062				7f
		B	1.448	—		0.080	0.088	0.112		28f
Methylmaleic anhydride (4b)		A	1.46	0.75						
		B	1.46			0.22				28g
Methyl acrylate (21a) ^g	-2.12 ^h	A	1.47	0.35 ⁱ						25a
		B				Not seen				
Diethyl maleate (21c)	-1.52 ^j	A				Not analyzed				
		B ^k	1.45	—		0.27	0.017 (2)	0.034 (2)	0.064 (2)	28j
Diethyl fumarate (21d)	-1.54 ^j	A				Not analyzed				
		B	1.45	—		0.27	0.017 (2)	0.034 (2)	0.064 (2)	28j
Acrylonitrile (21f) ^g	-2.17 ^j	A	1.45	0.37 ^j						25b
		B				Not seen				
Diethyl acetylenedicarboxylate	-1.28 ^m	A	1.43	0.163 ⁿ						26a
		B	1.45	0.325 ⁿ						26b
Diethyl azodicarboxylate	-0.56 ^o	A	1.48	0.564 ^p	0.115					27
		B				Not seen				

^aThe multiplicity of each coupling was 1, unless otherwise stated (number in parentheses). ^b $E_{1/2}$ in DMF on Hg.³⁵ ^cWith PBN- α (²H), this coupling disappeared and the A spectrum became hidden under the B spectrum. ^d E_{pc} from cyclic voltammetry in acetonitrile on Pt. ^eThe value for *N*-butylmaleimide is given. ^fIn DMF on Hg.³⁶ ^gThe reaction was run in neat substrate. ^h $E_{1/2}$ for ethyl acrylate in DMF on Hg.³ ⁱWith PBN- α (²H) the spectrum was a triplet, $a^{\text{N}}=1.48$ mT, of broad lines, $\Delta H_{pp}=0.16$ mT, which could not be further resolved. ^j $E_{1/2}$ in DMF on Hg.³⁷ ^kA partially resolved spectrum of **28j** has been published: $a^{\text{N}}=1.40$, $a^{\text{H}}=0.25$ mT. ^lWith PBN- α (²H) the spectrum was a triplet, $a^{\text{N}}=1.47$ mT, of broad lines, $\Delta H_{pp}=0.20$ mT, which could not be further resolved. ^mAs an ultrasound promoted emulsion in water.³⁸ ⁿWith PBN- α (²H) the spectrum was a triplet, $a^{\text{N}}=1.43$ mT, which could be further resolved by a forward-backward Fourier transformation, $a^{\text{D}}=0.054$ mT. ^o E_{rev} in acetonitrile on Pt. ^pWith PBN- α (²H) the spectrum showed $a^{\text{N}} 1.48$, $a^{\alpha\text{-H}} 0.087$ and $a^{\text{N}} 0.115$ mT; in addition a second spectrum belonging to an unidentified species was seen: $a^{\text{N}} 1.48$ and $a^{\text{N}} 0.32$ mT (1 N each).

see **24**) for the production of living polymers via neutral radical polymerization,¹⁶ except that after homolysis the active radical site and the aminoxyl radical are located within the same molecule. The bond susceptible to homolytic cleavage is indicated by a wavy line. A polymerization experiment showed that styrene was converted to a tough, transparent polymer (M_n 66 500, polydispersity 2.46) by stirring it for 6 h at 125 °C under argon with 0.1% of **23c** present, the recommended procedure^{16a} for testing this type of compounds as initiators. With 0.5% of **23c** as the initiator, a hard brittle polymer (M_n 67 400, polydispersity 1.88) was formed in 1.5 h under the same conditions. Comparison with literature data^{16b} for **24** shows that **23c** is considerably more efficient as an initiator. However, the polydispersities obtained^{16b} were considerably smaller, 1.2–1.4.

The reaction between PBN and other activated olefins. The photochemical reaction between PBN and other

cyclic activated olefins in dichloromethane gave rise to mixtures of type A and B spectra, as summarized in Table 3. With daylight as the source of photons, the reactions required 2–20 h for the development of resolved spectra of reasonable intensity, except in the case of maleic anhydride **4a**, where thermal generation of the species responsible for the B spectrum was observed.

The behaviour of maleimide **3a** was already described in the Introduction, and use of *N*-(²H)-maleimide **3d** affected only the 0.079 mT coupling constant of the B spectrum, giving a spectrum of eight broad, badly resolved lines which was well simulated by the parameters given in Table 3. The spectrum was somewhat obscured by the partial appearance of the B spectrum derived from the fully protonated compound (**3a**). We ascribe this to an ongoing photochemical reaction (see discussion below) producing protons which can exchange with **3d** and re-form **3a**. The addition of a deuterium source [O-

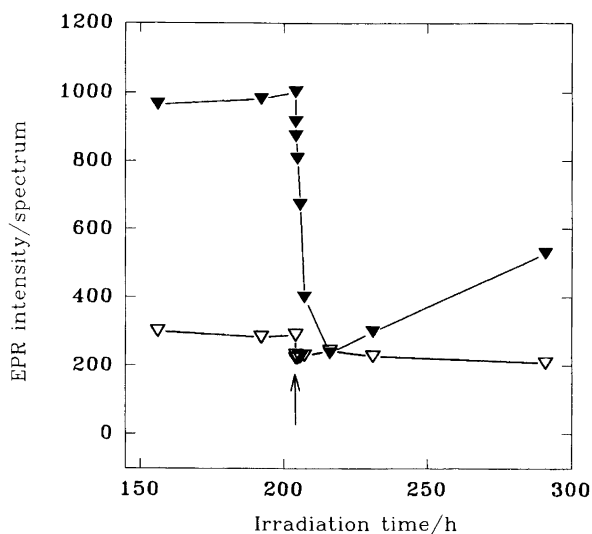


Fig. 6. EPR spectral intensity recorded from the solution of the experiment of Fig. 4 before and after the addition of *t*-BuNO. The arrow shows the time of addition of *t*-BuNO (to a final concentration of 0.7 mmol dm^{-3}). Empty triangles: spectrum A. Filled triangles: spectrum B.

(^2H)-1,1,1,3,3,3-hexafluoropropan-2-ol, 2% v/v] of similar *pK* as maleimide almost completely alleviated this difficulty.

The origin of the present study was the finding⁴ that *N*-cyanosuccinimide upon photolysis with PBN gave rise to a superposition of A–B type spectra. This was then suggested to reflect the existence of a pathway from *N*-cyanosuccinimide to *N*-cyanomaleimide under the prevailing reaction conditions. Repeated experimentation with both compounds eventually revealed that the sample of *N*-cyanosuccinimide contained 0.7% of *N*-cyanomaleimide, and that this low level was sufficient to account for the intensity of the A–B spectral superposition recorded. The formation of *N*-cyanomaleimide in the preparation of *N*-cyanosuccinimide, involving treatment of succinimide anion by BrCN ,¹⁷ can easily be understood in terms of concurrent bromination in the 3-position followed by elimination of HBr .¹⁸

The B spectrum from *N*-methylmaleimide (**3e**) even at the best resolution obtainable degenerated to a 5- or 6-line spectrum which could not be fully analyzed.

Maleic anhydride (**4a**) reacted spontaneously with immediate development of the B spectrum which then slowly decreased in intensity. The A spectrum appeared after daylight exposure for about 10 h and then remained at a constant level of intensity. Methylmaleic anhydride required light exposure for the development of weak A and B spectra, the species corresponding to the B spectrum being the more persistent one.

The use of an acyclic activated olefin, such as diethyl maleate (**21c**), gave an EPR spectrum which was not directly analyzable in terms of A and B spectra (Fig. 8a). However, when $\text{PBN-}\alpha(^2\text{H})$ was the substrate, it was seen that part of the spectrum responded as a PBN spin

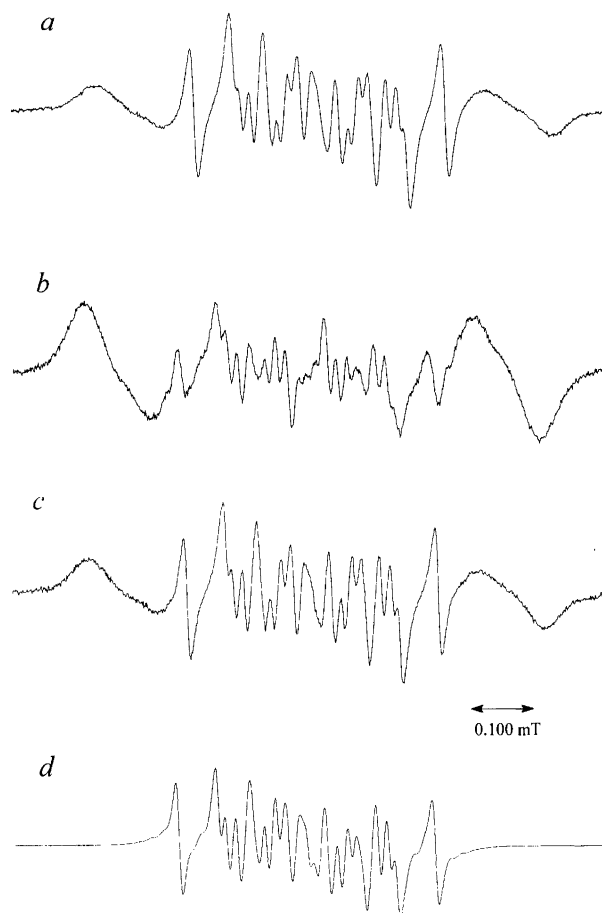


Fig. 7. EPR spectra (middle group of lines; number of accumulated spectra given in parentheses) recorded during the experiment shown in Fig. 6, taken (a) immediately before the addition of *t*-BuNO (5), (b) 12 h after the addition of *t*-BuNO and irradiation by daylight (17), (c) 80 h after the addition of *t*-BuNO and irradiation by daylight (14). The scale is the same for these spectra. The (d) spectrum is a simulation of a 1:1 superposition of the middle group of lines of the B spectrum from *N*-phenylmaleimide (linewidth 0.008 mT) and the spectrum of **20c** (linewidth 0.014 mT), using the parameters given in Tables 1 and 3.

adduct (change of the major 0.27 mT hydrogen coupling into a 0.041 mT deuterium coupling with a resultant narrowing of the spectrum) whereas the remaining part seemed largely unchanged (Figs. 8b and 8c). In this case, the A spectrum had disappeared after 20 h exposure time (Fig. 8d), and thus the B spectrum could be fully analyzed. Diethyl fumarate **21d** in a similar reaction gave almost identical spectra, but their rate of development was slower.

Monosubstituted olefins, like methyl acrylate **21a** and acrylonitrile **21f**, gave only A type spectra, assigned to species **25a** and **25b**, respectively, as supported by experiments in which $\text{PBN-}\alpha(^2\text{H})$ was used. An activated acetylene, diethyl acetylenedicarboxylate, gave two PBN spin adducts [as shown with $\text{PBN-}\alpha(^2\text{H})$ as the spin trap], presumably with structures **26a** and **26b**, and a similar spin adduct **27** [as shown with $\text{PBN-}\alpha(^2\text{H})$ as the

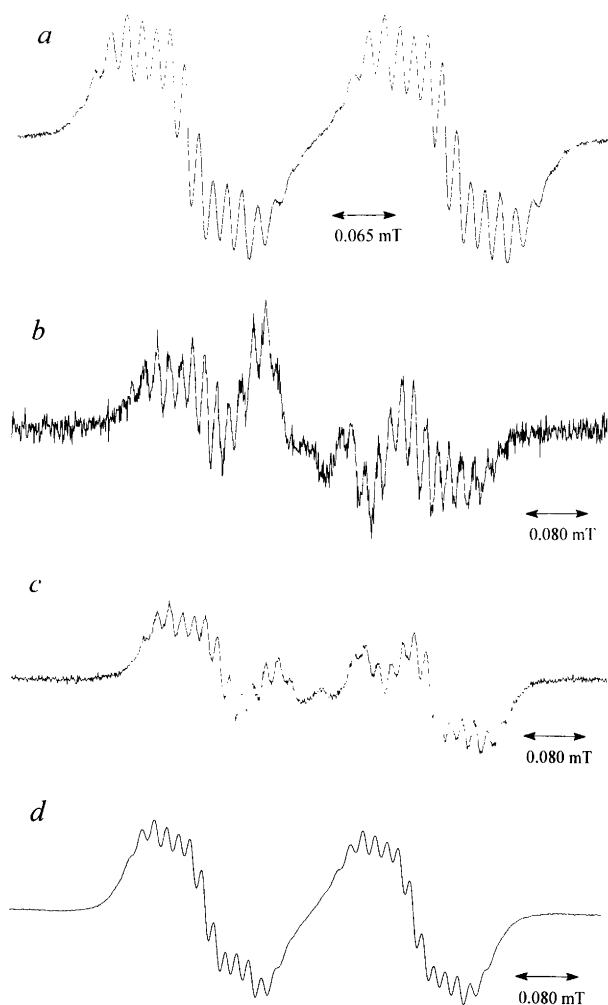
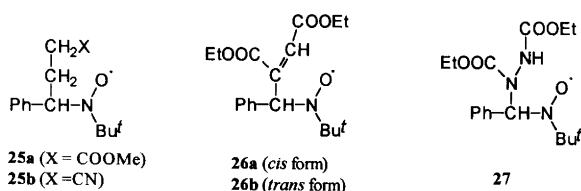


Fig. 8. The middle group of lines of the EPR spectrum recorded from a dichloromethane solution of diethyl maleate **21c** (0.25 mol dm^{-3}) and (a) PBN (0.2 mol dm^{-3}) after exposure to daylight for 20 h, or PBN- $\alpha(^2\text{H})$ (0.2 mol dm^{-3}) after exposure to daylight for (b) 0.5 h, (c) 1.5 h and (d) 20 h.

spin trap] was obtained from the diethyl azodicarboxylate, a PTAD analogue but much less reactive.

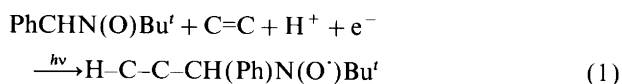


Photolysis of PBN and succinimide, N-methylsuccinimide, N-phenylsuccinimide or succinic anhydride with di-*t*-butyl peroxide in dichloromethane. Photolysis of di-*t*-butyl per-

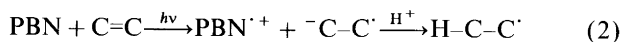
oxide or thermal decomposition of di-*t*-butyl peroxalate is known to produce *t*-BuO \cdot which can abstract hydrogen atoms adjacent to carbonyl functions in for example esters and amides.⁵ The radicals formed can be trapped by PBN. Thus the dihydro derivatives of activated olefins **3**, **3-H₂**, and **4a**, **4a-H₂** should be expected to undergo this type of reaction.

Photolysis of di-*tert*-butyl peroxide and succinimide (**3a-H₂**) or succinic anhydride (**4a-H₂**) in dichloromethane gave rise to EPR spectra predominantly derived from the spin adduct of *t*-BuO \cdot and PBN but also possessing a second component with the characteristics of type A spectra (Table 4). Since the persistency of *t*-BuO-PBN \cdot is limited, the second component was preferably analyzed after keeping the sample in the dark for at least 24 h. Owing to the strong interference of the spectrum of *t*-BuO-PBN \cdot it was not possible to detect any contribution present from type B spectra. *N*-Methylsuccinimide (**3e-H₂**) or *N*-phenylsuccinimide (**3c-H₂**) under these conditions did not show any sign of the A type spectrum.

Possible structure of radicals corresponding to spectra A and B. As concluded previously, spectra A should be assigned to radicals **7**, formally derived from a reductive coupling process between PBN and the activated olefin [eqn. (1)].



Such a reaction can be formulated according to a variety of mechanisms, but bearing in mind its photochemical nature, it is probable that a photochemical electron transfer (ET) is the initial step [eqn. (2)]. PBN* is a strong ET reductant [$E^0(\text{PBN}^{\bullet+}/\text{PBN}^*) = -2.7 \text{ V vs. SCE}$] and should transfer an electron to the activated olefins used in this study (see redox potentials in Table 3). This would supply a pair of radical ions, where protonation of the radical anion of the activated olefin would produce a reactive neutral radical [eqn. (2)]. Trapping of this radical by a second molecule of PBN gives a radical of type **7** [eqn. (3)].



The possible source of the proton in eqn. (2) will be discussed below.

The A type spectra from the cyclic activated olefins all have the characteristics of PBN spin adduct spectra. They responded to the use of $\alpha(^2\text{H})$ PBN in the predicted way, and the large $a^{\alpha\text{-H}}$ observed have precedents in the large $a^{\alpha\text{-H}}$ of the related dialkylaminoformyl adducts ($\text{R}_2\text{NCO-PBN}^\bullet$).^{4,5} The fact that the same spectra appear in conventional spin trapping experiments from the photolysis of di-*tert*-butyl peroxide with some of the dihydro olefins (**3-H₂**, **4a-H₂**), also provides evidence for structure **7**.

It is more problematic to assign a structure to the species giving rise to type B spectra. We have taken the

Table 4. Type A EPR spectra recorded from solutions of **3**-H₂ (0.2 mol dm⁻³), PBN (0.2 mol dm⁻³) and di-*tert*-butyl peroxide (0.7 mol dm⁻³) in dichloromethane, irradiated by UV light.

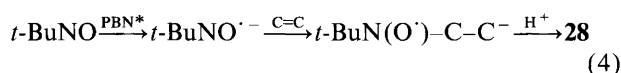
Dihydro compound		a^N/mT	$a^{\alpha\text{-H}}/\text{mT}$	a^H/mT
Succinimide 3a -H ₂	<i>t</i> -Bu ₂ O ₂ - <i>h</i> ν	1.44	0.64 (broad)	
	A spectrum from 3a	1.45	0.68	0.070
<i>N</i> -Phenylsuccinimide 3c -H ₂	<i>t</i> -Bu ₂ O ₂ - <i>h</i> ν		No A spectrum seen	
	A spectrum from 3c	1.44	0.63	0.060
<i>N</i> -Methylsuccinimide 3e -H ₂	<i>t</i> -Bu ₂ O ₂ - <i>h</i> ν		No A spectrum seen	
	A spectrum from 3e	1.43	0.66	0.055
Maleic anhydride 4a -H ₂	<i>t</i> -Bu ₂ O ₂ - <i>h</i> ν	1.47	0.81	0.067
	A spectrum from 4	1.46	0.81	0.062

behaviour of the very reactive dipolarophile, PTAD, as a first clue to the mechanism behind their formation. It reacted with PBN in a fast reaction (2–3 min) and gave *t*-BuNO, a well known spin trap, in 74% yield and dimer **16** (Scheme 2). In addition, the persistent *t*-butylurazolyl radical (**17**, R = *t*-Bu) was formed by trapping of the *t*-butyl radical, generated by photolysis of *t*-BuNO. The latter reaction could be achieved by the reaction of an authentic sample of *t*-BuNO and PTAD.

A related reaction (Scheme 4) took place upon irradiation of *t*-BuNO and activated olefins; again the reaction was mediated by addition of *tert*-butyl radical to the activated olefins, but now the intermediate neutral radical (**19**) is a reactive one and adds to a second molecule of *t*-BuNO to give spin adducts **20**. These had EPR spectra (Tables 1 and 2) which in all cases were different from the type B spectra obtained from the same series of compounds. Yet we propose that *t*-BuNO, somehow formed in very low concentration by interaction of PBN and the activated olefin, acts as a spin trap toward the neutral radical generated by the reactions of eqns. (2) and (3) or in some other way achieves the equivalent transformation by a reductive coupling process. This would give spin adducts of type **28**, similar to **20** but with the *tert*-butyl group replaced by a hydrogen atom.

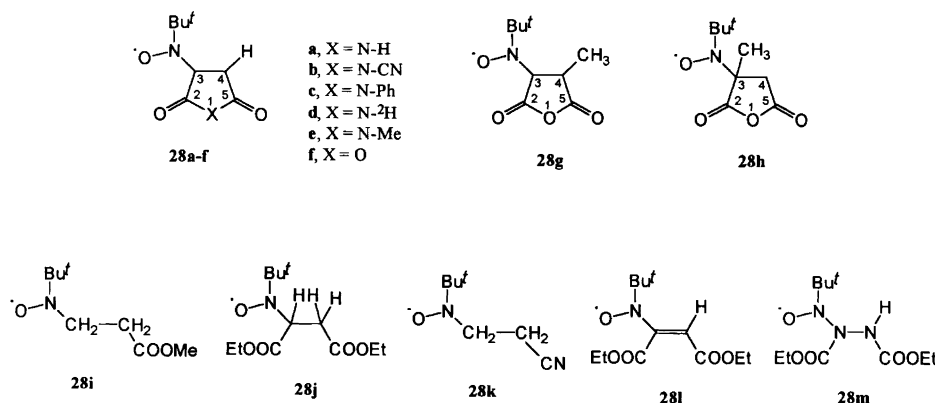
If we for a moment neglect the problem of the exact mode of formation of *t*-BuNO, it can be noted that this compound is relatively easy to reduce [$E^\circ(t\text{-BuNO}/t\text{-BuNO}^{\cdot-}) = -1.7\text{ V vs. SCE}$]¹⁹ and that its excited state does not possess reducing properties [$E^\circ(t\text{-BuNO}^{\cdot+}/t\text{-BuNO}^*) = 0.1\text{ V vs. SCE}$]²⁰ which makes ET from *t*-

BuNO* to any of the activated olefins in Table 3 impossible. Thus reductive coupling between *t*-BuNO and an activated olefin *alone* cannot be achieved photochemically, as shown by the results listed in Table 1. Another reaction, formation of radicals **20** or **22** by an entirely different mechanism, takes place instead. In the presence of PBN, however, *t*-BuNO can receive an electron from PBN* in a diffusion-controlled reaction (this step is exergonic by ca. 1 eV) and thus will give *t*-BuNO^{·-}, which might add as an anion to the olefinic double bond. Finally, protonation gives radical **28** [eqn. (4)].



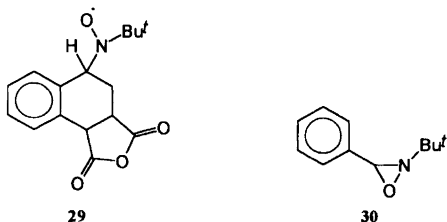
The EPR spectra of B type are in agreement with this assignment. Aminoxyls **28a–f** are all spin adducts of *t*-BuNO where the trapped radical has the X₂CH' structure; the EPR spectra of such radicals have $a^N \sim 1.45\text{ mT}$ and $a^H \sim 0.1\text{--}0.2\text{ mT}$.^{1b} Further couplings to other nuclei of the trapped radical are often seen; in the spectra of **28** the unusual situation that all such couplings are resolvable sometimes is at hand (**28a, c, d, f**). The fact that the B spectrum from methylsuccinic anhydride is a 3 × 2-line spectrum of $a^N = 1.46\text{ mT}$ and $a^H = 0.22\text{ mT}$ shows that the 3-methylsuccinic anhydride radical has been attached via the 4-position (i.e. structure **28g** is preferred over **28h**).

The development of B spectra seems to be reflected in the redox reactivity of the olefin, as expressed by their redox potentials. Diethyl maleate (–1.52 V) and diethyl



fumarate (-1.54 V) gave B spectra, whereas the less reactive methyl acrylate (-2.12 V) and acrylonitrile (-2.17 V) only gave A spectra. For the latter two compounds, the B type spectra have been recorded from **28i** and **28k** prepared in a different way:²¹ methyl acrylate, a^N 1.53, a^H 1.23 (2 H) mT; acrylonitrile, a^N 1.47, a^H 1.11 (2 H), $a^{H'}$ 0.06 (2 H) mT. If present, spectra of **28i** or **28k** would therefore be easily distinguished from the A-type spectra. The assignment of the B-type EPR spectrum from diethyl fumarate (Table 3) to **28j** receives support from the fact that this radical, prepared from the reaction of di-*tert*-butyl peroxalate, triethylsilane, diethyl 2-bromosuccinate and *t*-BuNO,²¹ had a similar EPR spectrum ($a^N=1.40$ mT, $a^H=0.25$ mT in benzene, cf. 1.45 and 0.27 mT in dichloromethane obtained here; the smaller couplings were not resolved in the earlier study).

In a study²² aimed at characterizing radicals in the copolymerization of styrene and **4a**, the latter compounds were allowed to react in ethylbenzene in the presence of *t*-BuNO. An EPR spectrum of a spin adduct with the assumed structure of **29**, formed from the Diels-Alder adduct of **4a** and styrene, was recorded. This spectrum was claimed not to be identical to that of **28f**, which was generated in an independent way but unfortunately not characterized. Several other spectra of similar type were described, all with a close relationship to that of **28f**. Since the conditions of light exposure were not defined, we presently refrain from an extended discussion. A recent paper has repeated and partly re-evaluated these results.¹³



Now, if *t*-BuNO is formed from PBN and is the origin of radicals **28**, why do we not see the parallel generation of radicals **20** or **22**? The experiment reported in Figs. 6 and 7 demonstrates that radical **28c** is rapidly consumed in a solution where *t*-BuNO is undergoing photolysis and that the EPR spectrum of **28c** is little influenced by this reaction. These findings can be explained as very rapid capture of *t*-Bu \cdot by **28c** to give a diamagnetic species. Trapping of carbon-centered radicals is a well known reaction of aminoxyls derived from nitroso compounds, proceeding with rate constants near the diffusion-controlled limit.^{11,23}

The next problem to solve is the mode of generation of *t*-BuNO. We cannot presently propose a detailed mechanism for its formation, but assume that the PTAD-PBN decomposition mechanism, initiated by the formation of cycloadduct **9** (Scheme 2), or some variety of it can be taken as a model. In this system, the yield

of *t*-BuNO was 74% after 2–3 min, and its involvement in the formation of the *tert*-butylurazoly radical **17** according to Scheme 3, left part, is therefore obvious.

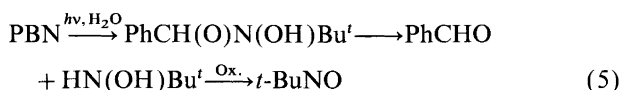
For the next system in order of reactivity, *N*-phenylmaleimide (as judged by the redox potential), the formation of cycloadduct **23c** was a very slow process under the conditions of the experiment described in Fig. 4. Compound **23c** was prepared in a thermal reaction requiring heating of PBN with *N*-phenylmaleimide in ethanol to 78 °C for 72 h, and was accompanied in the recrystallized state by about 1% of a radical exhibiting the same B spectrum as from the **3c**-PBN reaction in dichloromethane at room temperature in the dark and assigned to structure **28c**. In dichloromethane solution, the cycloadduct did not seem to produce radicals at room temperature or slightly above under thermal or photochemical conditions; only at temperatures around 125 °C was it reactive enough to sustain the polymerization of styrene. The intermediacy of the cycloadduct in the formation of **28c** is therefore doubtful, and other modes of formation of *t*-BuNO are open for discussion.

Thus we can only say presently that the reaction between PBN and a sufficiently activated olefin can proceed slowly in the thermal mode (or photochemically) to produce a very low concentration of *t*-BuNO which eventually is converted into radical **28**. The reaction is either mediated by the cycloadduct **23** or runs in parallel; there was no definitive support for either mode and we therefore leave this question open. Once *t*-BuNO is beginning to be formed in the presence of PBN, it can act as a trap for radicals formed via eqn. (2) and (3), or undergo reductive coupling [eqn. (4)] initiated by photo-ET from PBN* forming aminoxyls **28**. The fact that radicals **20** are not detected is probably due to the fact that radical **28** can act as an efficient trap for any *t*-Bu \cdot formed by photolysis of *t*-BuNO (Fig. 6).

A final problem regards the source of protons. Experiments designed to influence the B spectrum from **3c** by adding a source of deuterons, such as *O*-(2 H)-1,1,1,3,3,3-hexafluoropropan-2-ol, or by using (²H₂)dichloromethane as the solvent generally did not lead to any spectral changes. Only with a strong acid like (²H₂)sulfuric acid present was it possible to detect incorporation of deuterium atoms into aminoxyl **28c**. We conclude from these experiments that there is an internal source of acidic protons available in the system. A logical choice is the radical cation of PBN which is known to decompose rapidly giving *tert*-butyl cation, a strongly acidic species.^{3,24} Since the engine of all reactions leading to aminoxyls **7** and **28** is the ET step of eqn. (2), a strongly acidic proton source will be available under photochemical conditions. Experiments to test this assumption are underway.

Perspectives on the formation of t-BuNO from PBN. The photochemical degradation of PBN, presumably by intervention of its three-membered ring isomer, α -phenyl-*N*-

tert-butyloxazirane (**30**), has been long known.²⁵ Usually, this side-reaction only manifests itself by the appearance of the EPR spectrum of *t*-Bu₂NO'. The reaction was recently discussed²⁶ in the context of spin trapping by PBN in biological systems where the degradation of PBN to *t*-BuNO was assumed to occur via eqn. (5), a photochemically (including ambient light) induced hydrolysis mechanism. The detection of *t*-Bu₂NO' signals the simultaneous generation of NO, the powerful effects of which may alter biological functions in the system under study.



The results described above introduce a new pathway for the degradation of PBN to *t*-BuNO, namely the interaction of PBN with activated olefins. For olefins with redox potentials around -0.5 V (**3c**, **4a**), the reaction can even be spontaneous. Since quinones with potentials in a suitable range [as an example,²⁷ E° (benzoquinone/benzoquinone⁻) is -0.45 V vs. SCE] are ubiquitous in biological systems, this pathway may also be of importance in the latter context.

A similar cleavage of PBN to give *t*-BuNO occurred upon heating it with unsaturated fatty acid esters, like methyl oleate, with oxygen available to 80 – 170 °C.²⁸

Experimental

Materials. *N*-Cyanomaleimide (**3b**) and *N*-cyano-succinimide were prepared according to a literature procedure.^{29a} Recrystallized *N*-cyanosuccinimide contained 0.7% of *N*-cyanomaleimide (¹H NMR spectral analysis). Dimethyl- and phenylmaleic anhydride (**4c**) were available from an earlier study.^{29b} *N*-(²H)maleimide **3d** was prepared by distillation of maleimide, benzene and ²H₂O under a Dean–Stark water separator. After three additions of ²H₂O and complete removal of the solvent, the sample contained >98% *N*-(²H)maleimide. PBN- α -(²H) was available from an earlier study.³⁰ α ,*N*-Diphenyl-nitron was prepared as described.³¹ All other chemicals were of the highest commercial quality available.

Dichloromethane was of Suprasolv[®] and acetonitrile of Uvasol[®] quality (Merck AG).

Instruments and methods. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 spectrometer. Mass spectrometry was performed on a Jeol JMS SX-102 instrument. UV spectroscopy was performed by the HP-8452A UV–VIS diode array spectrophotometer, the kinetics being monitored by the HP89532K software package. All evaluations of rate constants were made by the SigmaPlot[®] program. Cyclic voltammetry was performed by the BAS-100 instrument, using an Ag/AgCl electrode as the reference, and with *i*R compensation. Potentials given and discussed in the text are given with the SCE as reference.

EPR spectra were recorded by the Upgrade Version

ESP 3220-200SH of a Bruker ER-200D spectrometer. The EPR experiments were performed as described earlier (100 kHz modulation frequency, microwave effect 0.4–1.25 mW, modulation amplitude 0.01–0.04 mT).^{3,4,20} Simulations were carried out by the public domain program WINSIM³² or Simfonia[®] from Bruker AG.

Light sources. Photolyses were performed in three ways: (i) in a photolysis cavity (ER 4104 OR), using light from the 50-W high-pressure Hg lamp from Bruker (ER 202). This method did not always give optimally resolved spectra, presumably due to slow diffusion in the sample tube. (ii) Externally by irradiation with a 300-W sun lamp (Osram Ultravitalux[®]), the light being filtered through a 5-cm water filter in a pyrex vessel. The distance between the lamp and the sample tube was ca. 10 cm. (iii) Externally by irradiation with diffuse daylight from a north-facing window. This was a slow procedure but gave maximally resolved spectra.

Reactions between *t*-BuNO and activated olefins. A solution of *t*-BuNO in dichloromethane (usually 1–3 mmol dm⁻³ but concentrations up to 100 mmol dm⁻³ were sometimes used in order to speed up the reaction) was made up by dissolving the appropriate amount of its dimer and allowing the solution to stand in the dark for 0.5–1 h in order to complete the equilibration to monomeric *t*-BuNO. The activated olefin was dissolved in a 0.70 ml aliquot of this solution in an amount corresponding to ca. 200 mmol dm⁻³. The solution was deaerated by bubbling with argon for 1.5 min in an EPR sample tube. The mixing procedure was performed in a darkened room and took about 2 min. Prepared in this way, the solution exhibited very weak paramagnetic activity. After a short light exposure (0.5–15 min, depending on the system under study and the light source employed), a well resolved EPR spectrum could be recorded. A slow gas evolution indicated that NO was formed. Longer light exposure gave stronger signals, but then the resolution sometimes was partially lost due to exchange processes.

Reaction between PBN and 4-phenyl-4H-1,2,4-triazoline-3,5-dione (PTAD). To a solution of 4.6 mg (26 μ mol) PTAD in 2.5 ml dichloromethane was added a solution of 6.0 mg (34 μ mol) PBN in 0.5 ml of dichloromethane, and the reaction was followed by UV spectroscopy. The initially red colour of the reaction mixture turned into green within 2 min. The kinetics of the decrease of the concentration of PTAD were monitored at 544 nm ($\epsilon = 137$ dm³ mol⁻¹ cm⁻¹) and gave a rate constant of 2.8 dm³ mol⁻¹ s⁻¹. The formation of 2-methyl-2-nitrosopropane was demonstrated by the presence of an absorption maximum at 678 nm in the final solution. This was verified by the appearance of a peak at 1.27 ppm in a ¹H NMR spectrum of the reaction products in CDCl₃ and comparison with authentic mat-

erial. The quantification of the yield of 2-methyl-2-nitrosopropane was further studied by NMR spectroscopy. A solution of 10.5 mg (60 μmol) PTAD and 11.5 mg (65 μmol) PBN in CDCl_3 was left until the reaction was completed. Then a known amount of acetonitrile was added as an internal standard, and the yield of 2-methyl-2-nitrosopropane (including its dimeric form) could be calculated to be 74%. The mass spectroscopic analysis of the reaction products showed the presence of a compound with a molecular mass of 530 which was assigned the structure **16**. This compound proved to be labile and was easily hydrolyzed, giving benzaldehyde and 4-phenylurazole (**18**, R=H) during attempts at further purification. Compound **16**: MS (EI): 530 (M, 43%), 265 (95%), 119 (100%). HRMS (EI): Found 530.1705. Calc. for $\text{C}_{30}\text{H}_{22}\text{N}_6\text{O}_4$ 530.1703.

Reaction between α ,N-diphenylnitrone and 4-phenyl-4H-1,2,4-triazoline-3,5-dione (PTAD). To a solution of 6.8 mg (39 μmol) PTAD in 1.5 ml acetonitrile was added a solution of 8.3 mg (42 μmol) α ,N-diphenylnitrone in 0.50 ml acetonitrile. The initially red colour of the reaction mixture turned into green within 10 s. A UV spectrum of the final solution showed the presence of an absorption maximum at 750 nm, indicating the formation of nitrosobenzene during the reaction. Quantification of the yield of nitrosobenzene by UV spectroscopy (ϵ_{750} in acetonitrile = $45 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) gave (three runs) an average yield of 78%. The mass spectroscopic analysis of the reaction products showed the presence of a compound with an identical mass spectrum and molecular mass as those of **16**.

Reaction between PBN and activated olefins. A solution of PBN or PBN- $\alpha(^2\text{H})$ (0.2 mol dm^{-3}), an activated olefin (0.2 mol dm^{-3}) and in some cases the appropriate additive in dichloromethane was kept in an EPR sample tube and irradiated. Depending on the system under study and the light source employed, paramagnetic activity in terms of spectra A and B appeared after a period of time (0.5–20 h). In the most reactive systems (**3c** and **4a**) type B spectra appeared also in the dark.

*Preparation of the cycloadduct **23c** between PBN and N-phenylmaleimide.* A stirred solution of 300 mg (1.73 mmol) PBN and 310 mg (1.75 mmol) N-phenylmaleimide in 10 ml ethanol was refluxed for 72 h.¹⁵ Evaporation of the solvent followed by recrystallization from dichloromethane/hexane gave colourless crystals of the cycloadduct **23c** in 70% yield.

A solution of 10 mg of **23c** in 0.7 ml dichloromethane was investigated by EPR spectroscopy and gave a strong signal of the B spectrum from **3c**. Heating this solution to ca. 40 °C did not affect the spectral intensity. When instead *p*-xylene was used as the solvent and the solution was heated to 100 °C, no EPR spectrum was detected. This led to a closer inspection of the NMR spectra and the presence of an impurity at the 1% level was revealed,

the following features being observed: ^1H NMR (CDCl_3): δ 2.87 (dd, J 18.3 Hz, 4.9 Hz), 3.33 (dd, J 18.3, 9.0 Hz), 5.57 (dd, J 9.0, 4.9 Hz). These data are consistent with the structure of **28c**.

*Cycloadduct **23c**.* M.p. 195–197 °C. ^1H NMR (CDCl_3): δ 1.08 (s, 9 H), 3.89 (dd, $J_{\text{H4,H3}}$ 7.8 Hz, $J_{\text{H4,H5}}$ 9.6 Hz, H4), 4.54 (d, $J_{\text{H5,H4}}$ 9.6 Hz, H5), 5.05 (d, $J_{\text{H3,H4}}$ 7.8 Hz, H3), 7.17 (dd, J = 8.3, 1.4 Hz, 2 H), 7.30–7.45 (m, 8 H). ^{13}C NMR (CDCl_3): δ 26.96 [$\text{C}(\text{CH}_3)_3$], 56.18 (C5), 59.66 [$\text{C}(\text{CH}_3)_3$], 67.08 (C4), 76.61 (C3), 126.23, 128.34, 128.94, 128.96, 128.99, 129.50, 131.78, 137.40, 172.53 (C8), 175.31 (C6). The assignments above were confirmed by HMQC, HMBC and NOESY. MS (EI): m/z 350 (M, 43%), 335 (25%), 294 (46%), 264 (66%), 173 (100%), 121 (63%).

*Polymerization of styrene with **23c** as the initiator.* Styrene (20 g) was heated to 125 °C under an argon atmosphere and 20 mg of cycloadduct **23c** added with magnetic stirring. After 6 h the mixture had become strongly viscous and was poured into a beaker. A tough, transparent polymer was left after cooling and standing for a few days, when all of the styrene had been consumed. A similar reaction with 10 g of styrene and 50 mg of **23c** gave a viscous mass already after 1.5 h, and the resulting polymer was hard and brittle.

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