

Oxiranylcarbiny radicals from Allyloxy Radical Cyclization: Characterization and Kinetic Information via ESR Spectroscopy¹

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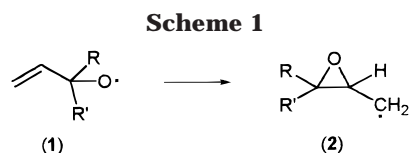
An ESR spin-trapping technique has been used for the detection of oxiranylcarbiny radicals as discrete reaction intermediates, formed via cyclization of allyloxy radicals. The latter were obtained by photolysis of the corresponding nitrites, which were generated directly via an exchange reaction between the appropriate allylic alcohols and *tert*-butyl nitrite (which also acts as the spin-trap). Experiments have also been conducted with the spin-trap 2,4,6-tribromonitrosobenzene, which has allowed a study to be made of the competition between ring closure and β -scission of a variety of allyloxy species.

Introduction

The formation of epoxides via a 1,3 intramolecular ring closure of the corresponding allyloxy radical (1) might be expected to be a facile process,³ but in only a few instances have the forecast products been characterized.^{4,5} The failure has been usually ascribed to the rapid fragmentation of the intermediate oxiranylcarbiny radical (2)^{5–8} by C–O bond cleavage to regenerate the allyloxy radical (a process that is expected to be preferred over C–C bond cleavage, except in cases where the resultant carbon radical is stabilized as a benzyl or an allyl radical^{5,6,9–12}).

It is perhaps not surprising that the oxiranylcarbiny radical itself has never been spectroscopically observed: a rate of $3.2 \times 10^{10} \text{ s}^{-1}$ has been reported⁶ for its cleavage at 25–30 °C (and a lower limit⁹ of $4 \times 10^8 \text{ s}^{-1}$ at 128 K). However, Galatsis^{13,14} has recently described the synthesis, in good yield, of α -iodo epoxides starting from tertiary and secondary allylic alcohols and using iodine as a trap for the intermediate oxiranylcarbiny radical, which implies that the ring-closed (oxiranyl) species has a discrete lifetime, under certain circumstances.

As described in a preliminary communication,¹ the spin-trapping ESR technique can be employed to char-



acterize the oxiranylcarbiny radical (2a), deriving from the 3-*exo-trig* closure of the 2-methylbut-3-en-2-oxyl radical (1a), as a discrete intermediate. The allyloxy radical (1a) was conveniently generated by photolysis of the corresponding nitrite [prepared via the facile exchange reaction between *tert*-butyl nitrite and the parent alcohol¹⁵ (3), reaction 1]



and the resulting oxiranylcarbiny radical trapped¹⁶ by *t*-BuONO to yield the nitroxide 4a [along with 5a]: a possible reaction mechanism for the formation of both radical species is outlined in Scheme 2. The aim of the present study was to obtain further and more detailed evidence on the existence of oxiranylcarbiny radicals as intermediates in the 1,3-*exo* ring closure process involving tertiary and secondary allyloxy radicals and to obtain information on the mechanism and the dependence on structure of the rates of formation and reaction of these cyclic species.

Results and Discussion

(a) Photolysis of Alkenyl Nitrites in the Presence of *tert*-Butyl Nitrite. (i) Results. Experiments were carried out by in situ photolysis ($\lambda > 250 \text{ nm}$) in an ESR spectrometer of acetonitrile solutions of allylic alcohols (typically 70 mM) in the presence of an excess of *tert*-butyl nitrite (ca. 115 mM), at different temperatures in the range 233–273 K. Optimum conditions were found to be at ca. 243 K.

All allylic alcohols employed led to the detection of ESR signals typified by a high value of the nitrogen hyperfine

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(1) For a preliminary account of some of this work, see: Grossi, L.; Strazzari, S. *J. Chem. Soc., Chem. Commun.* **1997**, 917.

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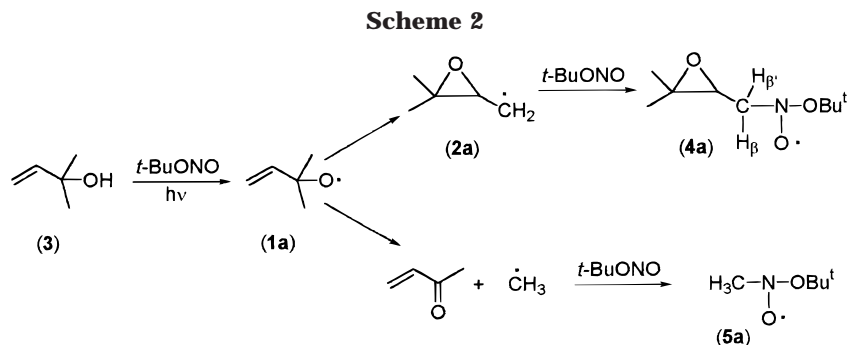


Table 1. ESR Hyperfine Splitting Constants (a/mT)^a of Nitroxide Radicals Generated by Photolysis of Allylic Nitrites Obtained from Allylic Alcohols and $t\text{-BuONO}$ ^b

Allyloxy	Nitroxide	$a(N)$	$a(\beta\text{-H})$		$a(\gamma\text{-H})$	$a(\delta\text{-H})$	g^c	Relative Conc. ^d
(1a) R, R' = CH ₃	(4a) R, R' = CH ₃	2.565	0.910 (1H)	0.560 (1H)	0.022	-	2.0053	(4a) : (5a) 87 : 13
	(5a) R = CH ₃	2.575	0.887 (3H)	-	-	-	2.0052	
		2.565	0.135 (² H)	0.080 (² H)	-	-	2.0053	
	(5a) R = CH ₃	2.575	0.887 (3H)	-	-	-	2.0052	
(1b) R = CH ₃ , R' = H	(4b) R = CH ₃ , R' = H	2.575	0.962 (1H)	0.575 (1H)	-	-	2.0053	(4b) : (5a) 80 : 20
	(5a) R = CH ₃	2.575	0.887 (3H)	-	-	-	2.0052	
(1c) R = Et, R' = CH ₃	(4c) R = Et, R' = CH ₃	2.572	0.925 (1H)	0.562 ₅ (1H)	0.025 (1H)	-	2.0053	(4c) : (5a) : (5b) 58 : 7 : 35
	(5a) R = Et	2.575	0.887 (3H)	-	-	-	2.0052	
	(5b) R = Et	2.570	0.821 (2H)	-	0.030 (3H)	-	2.0052	
(1d) R = Et, R' = H	(4d) R = Et, R' = H	2.550	0.995 (1H)	0.575 (1H)	-	-	2.0053	(4d) : (5b) 10 : 90
	(5b) R = Et	2.570	0.821 (2H)	-	0.030 (3H)	-	2.0052	
(1e) R = Pr, R' = H	(4e) R = Pr, R' = H	2.562	0.975 (1H)	0.525 (1H)	-	-	2.0053	(4e) : (5c) 6 : 94
	(5c) R = Pr	2.542	0.788 (2H)	-	0.030 (2H)	0.015 (3H)	2.0052	

^a ± 0.002 mT ^b typically at -30 °C ^c determined by comparison with DPPH (g 2.0037 \pm 0.0001) ^d at 246 K

splitting (ca. 2.5 mT) and characteristic β -proton and longer range splittings, which allowed us to assign them to the alkoxy nitroxides formed by the trapping of oxiranyl species and alkyl radicals (see Table 1). For example, 2-methylbut-3-en-2-ol (**3**) gave signals assigned

to the nitroxides **4a** and **5a** (see Figure 1a): for the former, nonequivalent β -proton splittings are consistent with the presence of the chiral center at the γ -position in the radical (that is, the β -protons are diastereotopic).¹⁷ To obtain further evidence for the assignment of **4a** and

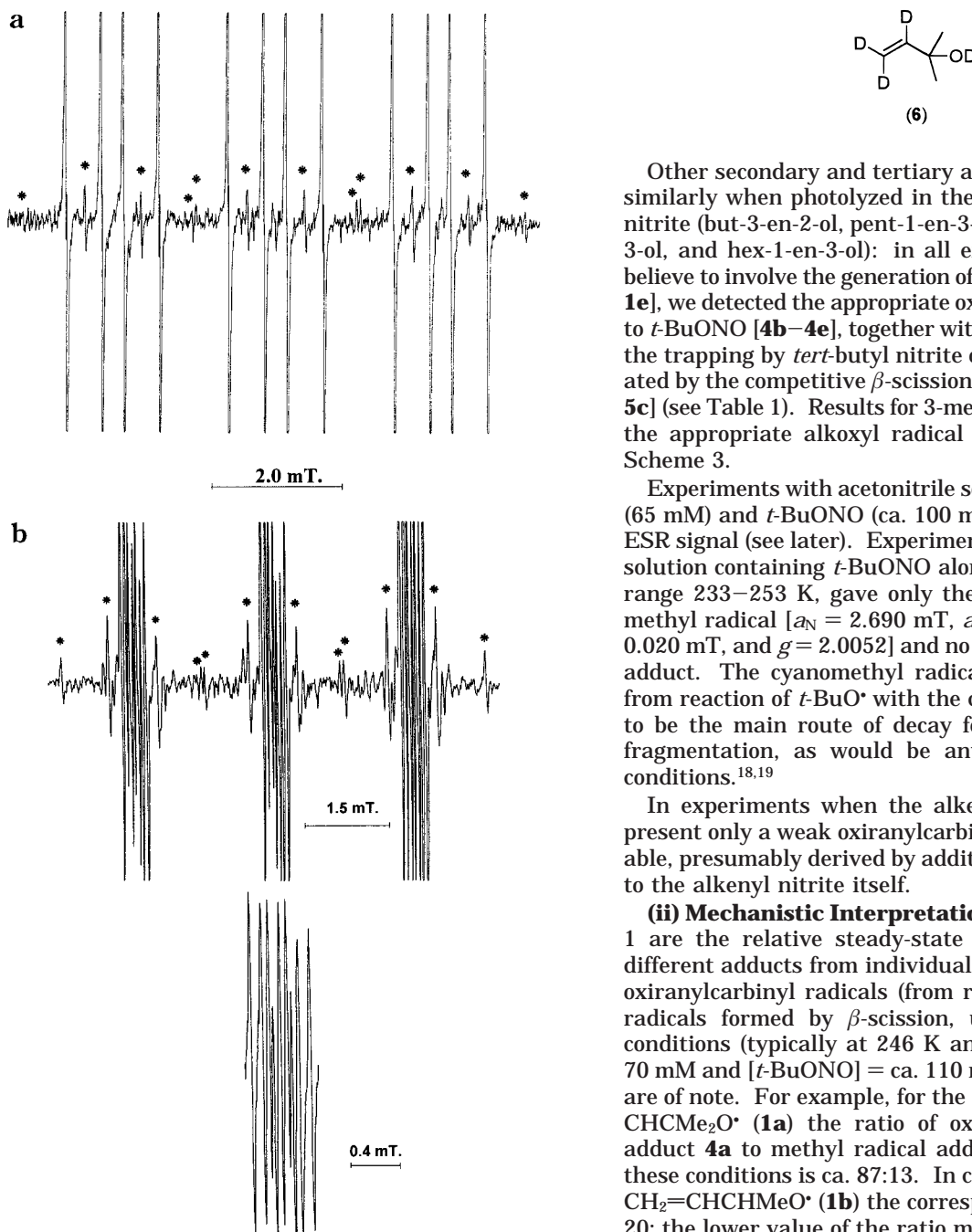
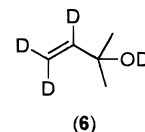


Figure 1. (a) ESR spectrum obtained in the photolysis of an acetonitrile solution of **3**, 70 mM, and *t*-BuONO, 115 mM, at 246 K, showing both radicals **5a*** and **4a**. (b) Upper part: ESR spectrum obtained in the photolysis of an acetonitrile solution of **6**, 70 mM, and *t*-BuONO, 115 mM, at 246 K, showing both radicals **5a*** and **7**. Lower part: Central group of radical **7** in expanded scale.

related species, a mixture of 2-methyl-[3,4,4-²H₃]but-3-en-2-ol-*d* (**6**) and *t*-BuONO was photolyzed, which led to the detection of the nitroxide **5a** as well as the deuterated nitroxide assigned the structure **7** (see Table 1), the latter characterized by a nitrogen splitting exactly matching that of **4a** and by two inequivalent deuterium splittings each ca. 1/6.5 that of the corresponding protons (see Figure 1b).

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Other secondary and tertiary allylic alcohols behaved similarly when photolyzed in the presence of *tert*-butyl nitrite (but-3-en-2-ol, pent-1-en-3-ol, 3-methylpent-1-en-3-ol, and hex-1-en-3-ol): in all experiments, which we believe to involve the generation of allyloxyl radicals [**1b**–**1e**], we detected the appropriate oxiranylcarbinyloxy adducts to *t*-BuONO [**4b**–**4e**], together with adducts derived from the trapping by *tert*-butyl nitrite of alkyl radicals generated by the competitive β -scission processes [**5a**, **5b**, and **5c**] (see Table 1). Results for 3-methylpent-1-en-3-ol, and the appropriate alkoxy radical **1c**, are illustrated in Scheme 3.

Experiments with acetonitrile solutions of allyl alcohol (65 mM) and *t*-BuONO (ca. 100 mM) gave no detectable ESR signal (see later). Experiments with an acetonitrile solution containing *t*-BuONO alone, in the temperature range 233–253 K, gave only the adduct of the cyanomethyl radical [$a_N = 2.690$ mT, $a_{2H\beta} = 0.525$ mT, $a_{N\gamma} = 0.020$ mT, and $g = 2.0052$] and no evidence of the methyl adduct. The cyanomethyl radical presumably derives from reaction of *t*-BuO[•] with the cosolvent; this appears to be the main route of decay for *t*-BuO[•] rather than fragmentation, as would be anticipated under these conditions.^{18,19}

In experiments when the alkenyl nitrite alone was present only a weak oxiranylcarbinyloxy adduct was detectable, presumably derived by addition of the alkyl radical to the alkenyl nitrite itself.

(ii) Mechanistic Interpretation. Also listed in Table 1 are the relative steady-state concentrations of the different adducts from individual allyloxyl radicals, i.e., oxiranylcarbinyloxy radicals (from ring closure) and alkyl radicals formed by β -scission, under a given set of conditions (typically at 246 K and with [alcohol] = ca. 70 mM and [*t*-BuONO] = ca. 110 mM). Several features are of note. For example, for the allyloxyl radical CH₂=CHCMe₂O[•] (**1a**) the ratio of oxiranylcarbinyloxy radical adduct **4a** to methyl radical adduct **5a** trapped under these conditions is ca. 87:13. In contrast, for the radical CH₂=CHCHMeO[•] (**1b**) the corresponding ratio is ca. 80:20; the lower value of the ratio may indicate that in the former, which from a statistical viewpoint might be expected to undergo relatively more rapid fragmentation, the *gem*-dialkyl substitution accelerates ring closure (an example of the Thorpe–Ingold effect;²⁰ see later). Notably, for CH₂=CHCMeEtO[•] (**1c**) the major radical detected

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Scheme 3

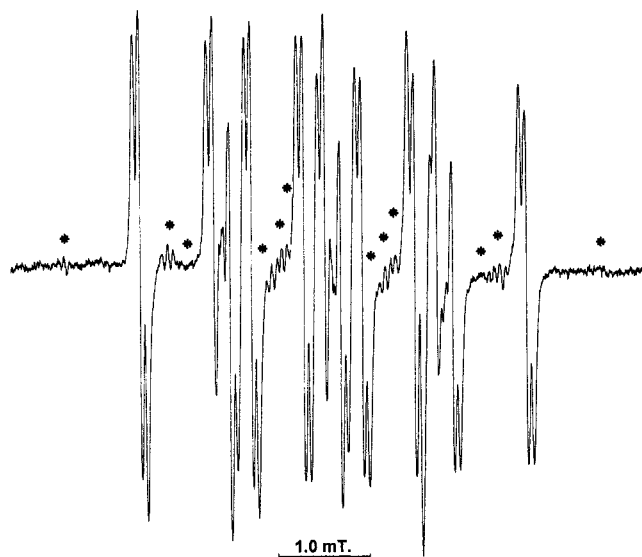
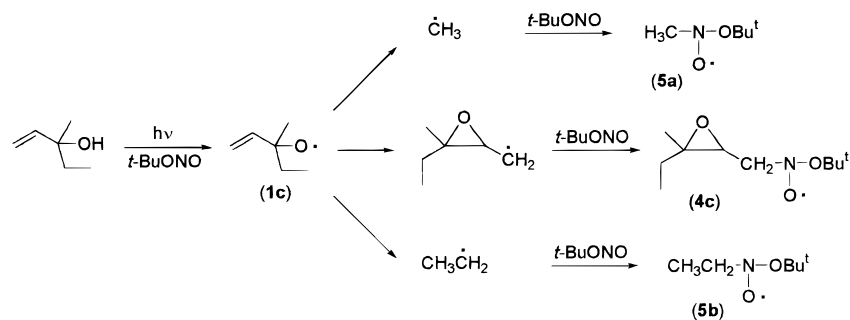


Figure 2. ESR spectrum obtained in the photolysis of an acetonitrile solution of **3**, 70 mM, *t*-BuONO, 110 mM, and TBNB, 72 mM, at 246 K, showing both radicals **8a** and **9a***

is the cyclized species **4c**, but the spectra indicate a greater propensity for fragmentation to give Et^\bullet rather than Me^\bullet , as might be expected (relative ratios ca. 58:35:7 for **4c**, **5b**, and **5a**). With the alkoxy radicals $\text{CH}_2=\text{CHCHEtO}^\bullet$ (**1d**) and $\text{CH}_2=\text{CHCHPrO}^\bullet$ (**1e**) the fragmentation process dominates, with ratios of ca. 90:10 and ca. 94:6, respectively under the conditions described above.

(b) Photolysis of Alkenyl Nitrite in the Presence of Other Spin-Traps. To verify that tertiary and secondary allyloxy radicals readily undergo 1,3-*exo* ring closure as proposed, we performed experiments with the spin-traps 2,4,6-tribromonitrosobenzene (TBNB) and 3,5-dibromo-4-nitrosobenzenesulfonic acid (DBNBS), which we would expect to behave as efficient traps for the oxiranylcarbiny radical intermediates, should they be formed. Allyloxy radicals were again generated by photolysis of the corresponding nitrites directly in an acetonitrile solution containing the nitroso spin-trap at a concentration (2.5–10 mM) such that radicals were trapped by the nitroso compound rather than the nitrite, from which no adducts were observed.

All the substrates in the presence of TBNB allowed us to detect signals which could be unambiguously attributed to the corresponding oxiranyl adducts together with the appropriate alkyl radical adducts (details are collected in Table 2): note again the nonequivalent splittings for diastereotopic protons (see Figure 2). No alkoxy adducts were observed from addition of the initial

allyloxy radicals to the trap; this must be due, at least in part, to the much shorter lifetime and lower stability of the (alkoxy) nitroxides formed in these cases. Related results were obtained in experiments with 2-methylbut-3-en-2-ol and but-3-en-2-ol and DBNBS (see Table 2).

Analogous experiments on acetonitrile solutions of allylic alcohol itself (65 mM) in the presence of *t*-BuONO (ca. 100 mM) and TBNB (25 mM) led to the detection solely of a signal with [$a_{\text{N}} = 1.365$ mT, $a_{2\text{H}\beta} = 0.935$ mT, $a_{2\text{H-meta}} = 0.055$ mT, and $g = 2.0061$]. This cannot characterize the trapping of the appropriate unsubstituted oxiranylcarbiny radical, for which nonequivalence of the β -protons would be expected; its origin is described later.

It is notable that the radicals detected are not those that would have been observed had an "ene" reaction taken place between the nitroso spin-trap and the allylic substrates²¹ followed by oxidation of the resultant hydroxylamine.

(c) Kinetic Studies. While rate constants for ring opening of the oxiranylcarbiny radical have been estimated,^{6,9} there is no reliable estimate for the reverse, ring-closing reaction. Our objective was to gain information about this or, at least, the relative rates of β -scission and ring closure.

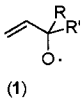
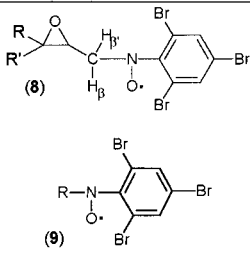
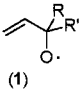
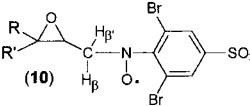
The approach taken has involved analysis of appropriate spin-trapping experiments with TBNB, which gives more persistent adducts of both alkyl and oxiranylcarbiny radicals than *t*-BuONO; this trap, which allows preparation of solutions at known concentrations, is also less UV-sensitive than the nitrites. Furthermore, the rates of trapping of alkyl radicals by aromatic nitroso compounds of this type are known.²²

Kinetic analysis is based on the results obtained for trapping of radicals **2a** and methyl, from $\text{CH}_2=\text{CHCMe}_2\text{O}^\bullet$ (**1a**), with TBNB [to give **8a** and **9a**] over a range of temperatures (233–266 K) and at a given temperature, for a range of TBNB concentrations (2.7–9.6 mM). For example, in a set of experiments with fixed trap concentration (7.2 mM), the observed ratios of the adducts [**8a**:**9a**] varied steadily from 49:1 (at 233 K) to 4.6:1 at 266 K (see Table 3); raising the temperature clearly increases the proportion of fragmentation, as might be anticipated, since this would be expected to have the higher activation enthalpy. In a separate set of experiments at 246 K, increasing the concentration of spin-trap leads to an

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Table 2. ESR Hyperfine Splitting Constants (a/mT)^a of Nitroxide Radicals Generated by Photolysis of Allylic Nitrites in the Presence of TBNB or DBNBS^b

Allyloxy	Spin Trap	Nitroxide	$a(N)$	$a(\beta-H)$	$a(2H-meta)$	g^c
	TBNB					
(1a) R, R' = CH ₃		(8a) R, R' = CH ₃	1.290	1.050 (1H)	0.865 (1H)	2.0062
		(9a) R = CH ₃	1.330	1.205 (3H)	-	2.0061
(1b) R = CH ₃ , R' = H		(8b) R = CH ₃ , R' = H	1.285	0.970 (1H)	0.785 (1H)	2.0062
(1c) R = Et, R' = CH ₃		(8c) R = Et, R' = CH ₃	1.285	1.025 (1H)	0.920 (1H)	2.0062
		(9b) R = Et	1.340	1.105 (2H)	-	2.0061
(1d) R = Et, R' = H		(8d) R = Et, R' = H	1.282	0.975 (1H)	0.775 (1H)	2.0062
		(9b) R = Et	1.340	1.105 (2H)	-	2.0061
(1e) R = Pr, R' = H		(8e) R = Pr, R' = H	1.283	0.985 (1H)	0.775 (1H)	2.0062
		(9c) R = Pr	1.327	1.035 (2H)	-	2.0061
	DBNBS					
(1a) R = R' = CH ₃		(10a) R = R' = CH ₃	1.287	1.020 (1H)	0.905 (1H)	2.0062
(1b) R = CH ₃ , R' = H		(10b) R = CH ₃ , R' = H	1.285	0.980 (1H)	0.770 (1H)	2.0062

^a ± 0.002 mT ^b typically at 246 K ^c determined by comparison with DPPH (g 2.0037 \pm 0.0001)

Table 3. Variation of the Ratio of the Radical Adducts [9a]/[8a] in Experiments on Solutions of 3, *t*-BuONO, and TBNB as a Function of Temperature at Fixed Spin-Trap Concentration (72 mM)

temperature (K)	[9a]/[8a] ^a
233	0.020
246	0.075
256	0.124
266	0.219

^a ± 0.005 .

increase in the proportion of oxiranylcarbinyl radical trapped; see Table 4.

Scheme 4 sets out the reactions which are believed to be involved in the process. It is believed that radical-

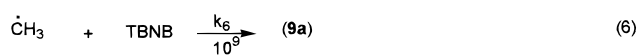
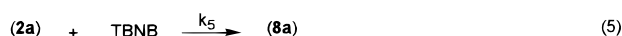
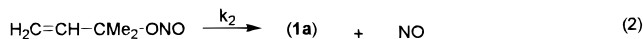
radical termination of carbon-centered radicals [i.e., reactions 7, 8, and 9] and carbon-centered radical addition to nitroxides are relatively unimportant under our reaction conditions. [This reflects the very low steady-state concentrations of carbon-centered radicals ($< 10^{-7}$ mol dm⁻³) and low concentration of nitroxides (ca. 10^{-6} mol dm⁻³) compared with the trap TBNB (10^{-2} – 10^{-3} mol dm⁻³) especially since addition to the latter is very fast ($k \sim 10^8$ dm³ mol⁻¹ s⁻¹). Steady-state analysis for Me[•] and radical 2a predicts a relationship for the ratio of their respective adducts [9a]/[8a] as shown in eq 1. (Inclusion of addition of the alkoxy radical to the trap in the steady-state analysis does not affect the ratio of adducts predicted.) Thus a plot of [9a]/[8a] versus [TBNB]⁻¹

Table 4. Variation of the Ratio of the Radical Adducts [9a]/[8a] in Experiments on Solutions of **3**, *t*-BuONO, and TBNB as a Function of Spin-Trap Concentration at Constant Temperature (246 K)

[TBNB] × 10 ⁻³ (mol dm ⁻³)	[9a]/[8a] ^a
2.7	0.099
3.2	0.095
4.2	0.087
5.2	0.079
7.2	0.076
7.9	0.074
9.3	0.071
9.6	0.070

^a ± 0.005.

Scheme 4



should give a straight line plot with an intercept of k_4/k_{3a} and a slope of $k_4k_{3b}/k_{3a}k_5$. It is interesting to note that, if the cyclization of the allyloxy radical is irreversible, then the ratio of the adducts would be independent of trap concentration, contrary to our observations.

$$\frac{[\text{9a}]}{[\text{8a}]} = \frac{k_4}{k_{3a}} \left(1 + \frac{k_{3b}}{k_5[\text{TBNB}]} \right) \quad (\text{eq 1})$$

When the results described above for variation of adduct ratios with trap concentration at 246 K are plotted in this manner, excellent agreement is observed (see Figure 3). Analysis of these data (see Table 4) gives the slope and intercept as $1.1 \times 10^{-4} \text{ mol dm}^{-3}$ and 5.9×10^{-2} , respectively. The value of k_5 , the rate of trapping of the oxiranylcarbiny radical, can be estimated as $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from spin-trapping experiments with DBNBS,²² which leads to a value of k_{3b} , the rate of ring opening of the epoxide, of $1.9 \times 10^6 \text{ s}^{-1}$. The ratio of fragmentation to cyclization of the alkoxy radical, k_4/k_{3a} , is 5.9×10^{-2} , showing that the rate constant for cyclization is significantly greater than that of fragmentation (β -scission) for this species. Rate constants for the β -scission of allyloxy radicals are not available, but values have been reported for the related fragmentation of the cumyloxy radical ($k = 1.25 \times 10^6 \text{ s}^{-1}$ at 300 K in chlorobenzene).²³ On the assumption that a rate of ca. 10^6 s^{-1} would be expected for the β -scission of the allyloxy radical (**1a**) (i.e., rapid due to the formation of the conjugated ketone) the estimated rate of cyclization is $1.7 \times 10^7 \text{ s}^{-1}$.

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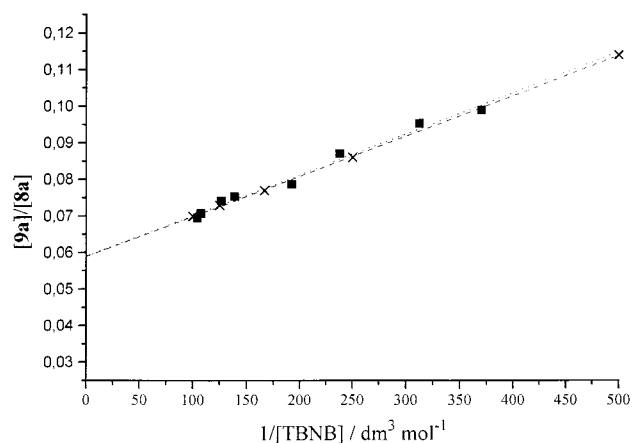


Figure 3. [9a]/[8a] ratios vs $1/[\text{TBNB}]$ ($\text{dm}^3 \text{ mol}^{-1}$) in experiments on an acetonitrile solution of **3**, 70 mM, *t*-BuONO, 110 mM, and TBNB at 246 K; ■ indicates the experimental data; × indicates data calculated by means of a kinetic modeling using the mechanism of Scheme 4 and the rate constants determined from the steady-state analysis.

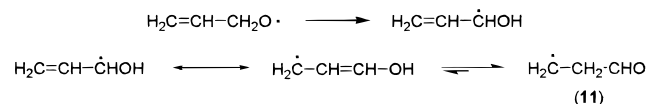
Computer kinetic modeling of the mechanism shown in Scheme 4 using the rate constants determined from the steady-state analysis (other rate constants used are given in Scheme 4) also gives an excellent fit to the experimental data (see Figure 3).

Conclusions

Allyloxy radicals have been shown to undergo a rapid reversible cyclization to give oxiranylcarbiny radicals, as well as β -scission yielding alkyl radicals and a conjugated ketone or aldehyde: relative rates of cyclization and fragmentation of the allyloxy radicals depend crucially upon both the extent and type of alkylation at the α -carbon. For the α, α -dialkylated alkoxy radical $\text{CH}_2=\text{CH}-\text{CMeEtO}^\bullet$ (**1c**), loss of Et^\bullet is much faster than loss of Me^\bullet , suggesting that, as expected, stability of the radical fragment is important in determining the relative rate of β -scission. As judged by the increase in the ratio of oxiranylcarbiny to alkyl radicals trapped [compare that observed for $\text{CH}_2=\text{CH}-\text{CMe}_2\text{O}^\bullet$ (**1a**) with that for $\text{CH}_2=\text{CH}-\text{CHMeO}^\bullet$ (**1b**)], it appears that dialkylation at the α -carbon significantly increases the rate of cyclization to the oxiranylcarbiny radical (since dialkylation would certainly not be expected to reduce the rate of fragmentation). This is apparently a further example of the *gem*-dialkyl effect.²⁰

For radical **2a** from $\text{CH}_2=\text{CHCMe}_2\text{O}^\bullet$, the rate constants of the ring-opening reaction ($1.9 \times 10^6 \text{ s}^{-1}$) and the reverse ring-closing reaction ($1.7 \times 10^7 \text{ s}^{-1}$) have been estimated. It is notable that the predicted rate of ring opening for the oxiranylcarbiny radical **2a** is substantially lower than that predicted⁹ for the nonmethylated analogue (estimated as $1 \times 10^8 \text{ s}^{-1}$). Evidently alkylation at the α -carbon of the alkoxy radical (C_3 in the cyclized radicals) has a dramatic effect on the rates of reaction of these species, which may arise in one or more of at least three possible ways. First, the *gem*-dialkyl effect might be expected to increase dramatically the rate of cyclization of the alkoxy radical (as noted earlier).²⁰ Second, dialkylation might also be expected to reduce the rate of ring opening of the oxiranylcarbiny species. Third, dialkylation would also prevent the 1,2-H shift which has been suggested previously for the unsubstituted allyloxy

radical ($\text{CH}_2=\text{CH}-\text{CH}_2\text{O}^\bullet$).^{24,25} This reaction, for which k may well be on the order²⁶ of 10^6 s^{-1} , provides an irreversible reaction of the allyloxy radical which may account for the lack of detection of the corresponding oxiranylcarbonyl species here and elsewhere.²⁵ Indeed, the observation of a different free radical (**11**) trapped from allyloxy itself with TBNB can be attributed to the occurrence of a rapid 1,2-H shift, followed by trapping at the methylene group.



Experimental Section

Materials. The allylic alcohols were commercial products and used as received, unless the purity was less than 98%, necessitating distillation. The *tert*-butyl nitrite and the 2-methyl-3-buten-2-yl nitrite were prepared following the standard procedure reported in the literature²⁷ and distilled under vacuum before use. The DBNBS was prepared starting from the 3,5-dibromosulfanilic acid oxidized in a mixture of glacial acetic acid, aqueous hydrogen peroxide, and anhydrous sodium acetate, following the procedure described by Kaur et al.²⁸ Similarly, the 2,4,6-tribromonitrosobenzene was prepared by adding 2,4,6-tribromoaniline to a mixture of glacial acetic acid, aqueous hydrogen peroxide, and concentrated sulfuric acid as reported by Holmes et al.²⁹

2-Methyl[3,4,4-²H₃]but-3-en-2-ol-d (6). 2-Methyl[4-²H]-but-3-yn-2-ol-d (2.0 g, 0.024 mol) was reduced with 1.2 g (0.029

mol) of LiAlD_4 , as selective reducing agent, according to the procedure reported³⁰ for the [4-²H]prop-2-yn-1-ol. The purified product was obtained as an oil by distillation (bp 97 °C; 1.4 g, 64.7%): ¹H NMR (CDCl_3 , 300 MHz) δ 1.21 (6H, s, CH_3); ¹³C NMR (CDCl_3 , 75.5 MHz) δ 29.1 (CH_3), 69.5 (C, CMe_2OD), 110.1 (quintet, CD_2), 145.7 (t, CD); HRMS calcd for $\text{C}_5\text{H}_6\text{D}_4\text{O}$, 90.0979; found, 90.0964.

2-Methyl[4-²H]but-3-yn-2-ol-d. 2-Methylbut-3-yn-2-ol (3.3 g, 0.039 mol) was dissolved in anhydrous Et_2O in the presence of sodium methoxide (3.3 g, 0.080 mol). The reaction mixture was stirred, refluxed under an N_2 atmosphere for 2 h, and subsequently quenched with 10 mL of D_2O . The mixture was extracted with Et_2O , and the organic layer was dried (Na_2SO_4) and concentrated in vacuo. The purified product was obtained as an oil by distillation (bp 104 °C; 3.2 g, 95.3%): ¹H NMR (CDCl_3 , 300 MHz) δ 1.55 (6H, s, CH_3); ¹³C NMR (CDCl_3 , 75.5 MHz) δ 31.2 (CH_3), 64.9 (C, CMe_2OD), 70.1 (t, CD), 88.9 (C, alkine); the ¹H NMR analysis showed complete deuterium incorporation; HRMS calcd for $\text{C}_5\text{H}_6\text{D}_2\text{O}$, 86.0699; found, 86.0672.

ESR Experiments. An oxygen-free acetonitrile solution containing allylic alcohol and *t*-BuONO in excess was continuously flowed (flow rate 0.1–0.6 mL/min) through a flat quartz cell (0.3 mm optical path length) inside an ESR cavity and directly irradiated with an OSRAM HBO 500W/2 high-pressure mercury lamp. A Varian E-104 spectrometer equipped with a variable-temperature apparatus was used.

ESR spectra in the experiments with the 2,4,6-tribromonitrosobenzene were recorded on a Bruker ESP 300 equipped with a X-band microwave bridge, 100 kHz modulation, and a variable-temperature apparatus. Oxygen-free acetonitrile solutions containing the spin-trap and the allylic nitrites were introduced in a sample quartz tube that was sealed and then analyzed in static condition directly in the cavity of the ESR spectrometer; the photolysis was carried out with the unfiltered output of an Hanovia 977B-1 1KW mercury–xenon compact arc lamp. Relative radical concentrations were obtained by means of a computer simulation.

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