# EPR studies of the formation and transformation of isomeric radicals $[C_3H_5O]^{\cdot}$. Rearrangement of the allyloxyl radical in non-aqueous solution involving a formal 1,2-hydrogen-atom shift promoted by alcohols

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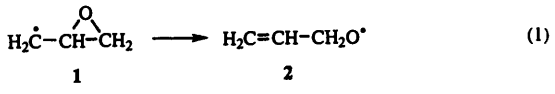
**At 220 K in cyclopropane solvent, hydrogen-atom abstraction from allyl alcohol by Bu$^t$O$^{\cdot}$, EtO$^{\cdot}$, PhMe$_2$CO$^{\cdot}$, (Me$_3$Si)$_2$N$^{\cdot}$ or triplet-state acetone gives the 1-hydroxyallyl radical 3 as a *ca.* 3:1 mixture of the *syn*- and *anti*-isomers. In contrast, the allyloxyl radical does not react with allyl alcohol to bring about abstraction of hydrogen, but instead undergoes a more rapid alcohol-promoted rearrangement to give 3 as a *ca.* 1:1 mixture of the *syn*- and *anti*-forms. 2-Methylallyl alcohol, ethanol and propan-2-ol also induce this formal 1,2-H-atom shift in the allyloxyl radical. In the presence of ethan[$^2$H]ol, both 3 and (3-*O*D) are formed and as [EtOD] is increased from 0.3 to 3.6 mol dm$^{-3}$ [3-*O*D]/[3] first passes through a maximum value of *ca.* 1 and then decreases to 0.38. It is proposed that there is more than one mechanism for the alcohol-induced rearrangement of the allyloxyl radical, one that involves assisted migration of hydrogen from the α-carbon atom to the oxygen atom and another that results in incorporation of deuterium from the EtOD. The importance of the latter mechanism decreases at high alcohol concentrations and this behaviour is thought to be related to the extent of association of the alcohol by hydrogen-bonding. The allyloxyl radical was generated by UV photolysis of allyl *tert*-butyl peroxide and by ring opening of the oxiranylmethyl radical, derived from epibromohydrin or epichlorohydrin by halogen-atom abstraction. *Ab initio* molecular orbital calculations predict that an unassisted 1,2-H-atom shift in the allyloxyl radical will involve a very large activation energy. The alcohol is believed to serve a dual function in promoting the rearrangement: first, to increase the acidity of the α-CH$_2$ group by hydrogen-bonding to the oxygen atom of the allyloxyl radical and, secondly, to provide a basic oxygen atom to facilitate the transfer/removal of a protic α-hydrogen atom.**

It is well established[1] that the oxiranylmethyl radical **1** undergoes very rapid regioselective ring opening to give the allyloxyl radical **2** and there is now evidence for the reversibility of this type of β-scission process.[2] The rate constant for ring opening of **1** [eqn. (1)] has been estimated to be $>4 \times 10^8$ s$^{-1}$ at 298 K



(1)

**1** **2**

and the oxiranylmethyl radical is too short-lived with respect to β-scission to allow its EPR spectrum to be detected in solution, even in liquid propane at 128 K.[3] Rather, it is the spectrum of the 1-hydroxylallyl radical **3** that has been observed during continuous generation of **1** in non-aqueous media and, under these conditions, the radical **3** was thought to arise by abstraction of hydrogen from allyl alcohol [eqn. (2)], itself formed by

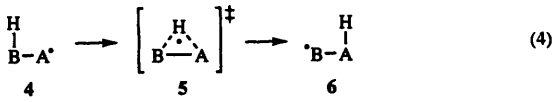
$$H_2C{=}CH{-}CH_2OH \xrightarrow[-XH]{X^{\cdot}} H_2C{=}CH{-}\dot{C}HOH \quad (2)$$

**3**

hydrogen-atom transfer to the allyloxyl radical **2**.[3,4] A 1,2-hydrogen-atom shift in the allyloxyl radical [eqn. (3)] as an

$$H_2C{=}CH{-}CH_2O^{\cdot} \longrightarrow H_2C{=}CH{-}\dot{C}HOH \quad (3)$$

alternative route to **3** was rejected, because there appear to be no authenticated examples of unimolecular rearrangements of the type **4** ⟶ **6**.[5] Theoretical calculations indicate that such



(4)

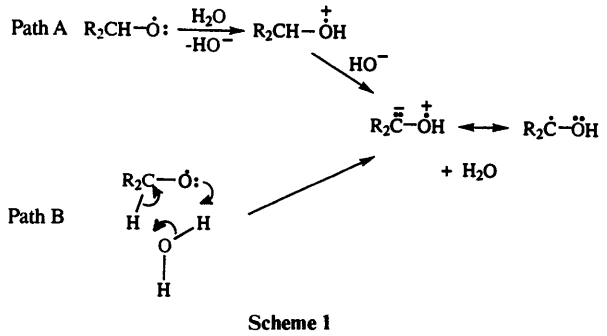
**4** **5** **6**

processes will be associated with high activation energies, implying that other uni- and bi-molecular reactions open to **4** will take place in preference to the rearrangement process (4) under normal conditions. In particular, the barriers to the exothermic 1,2-migration of a hydrogen atom from carbon to oxygen in the methoxyl[6,7] and ethoxyl[8] radicals in the gas phase [eqn. (5; R = H or Me)] have been calculated by *ab initio*

$$RCH_2O^{\cdot} \longrightarrow R\dot{C}HOH \quad (5)$$

molecular orbital methods to be 151 and 112 kJ mol$^{-1}$, respectively. An empirical estimate of 109 kJ mol$^{-1}$ has been made for the barrier to 1,2-H-atom shift in the methoxyl radical.[9]

However, there is compelling evidence that, in aqueous solution at room temperature, primary and secondary alkoxyl radicals are rapidly transformed into the corresponding α-hydroxyalkyl radicals in a process that involves the participation of water, it was thought possibly as depicted in Scheme 1 where the pathways A and B differ only in the timing of the proton




**Scheme 1**

**Table 1** EPR parameters for *syn*- and *anti*-isomers of substituted allyl radicals $H_2C{=}C(R){-}\dot{C}HY$ in cyclopropane at 220 K

| | | | | Hyperfine splittings/G | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Radical | Y | R | *g*-Factor | $H^1_{syn}$ | $H^1_{anti}$ | R | $H^3_{syn}$ | $H^3_{anti}$ | Y |
| **3S**[a] | OH | H | 2.002 98 | — | 13.84 | 2.98 (1 H) | 13.38 | 13.84 | 0.95 (1 H) |
| **3A**[a] | OH | H | 2.003 07 | 13.20 | — | 3.43 (1 H) | 13.20 | 14.28 | 1.04 (1 H) |
| **7S**[b] | OMe | H | 2.002 96 | — | 14.17[c] | 3.15 (1 H) | 13.18 | 13.64[c] | 1.43 (3 H) |
| **7A**[b] | OMe | H | 2.003 04 | 13.11[d,e] | — | 3.62 (1 H) | 13.07[d] | 13.98[e] | 1.12 (3 H) |
| **8S**[f] | OH | Me | 2.002 67 | — | 13.11 | 2.52 (3 H) | 12.60 | 14.15 | 0.88 (1 H) |
| **8A**[f] | OH | Me | 2.002 73 | *g* | — | 2.85 (3 H) | *g* | *g* | 1.05 (1 H) |
| **11S**[h] | $OSiMe_3$ | H | 2.002 99 | — | 14.31[c] | 3.10 (1 H) | 13.35 | 13.83[c] | — |
| **11A**[h] | $OSiMe_3$ | H | 2.003 05 | 13.65[d] | — | 3.45 (1 H) | 12.60[d] | 14.25 | — |

[a] The concentration of allyl alcohol was 2.4 mol $dm^{-3}$; when it was reduced to 0.6 mol $dm^{-3}$ the coupling constants were essentially unchanged. [b] Data at 213 K taken from ref. 21; the solvent is $CFCl_3$. [c] Assignment of splittings from $H^1_{anti}$ and $H^3_{anti}$ could be reversed. [d] Assignment of splittings from $H^1_{syn}$ and $H^3_{syn}$ could be reversed. [e] Assignment of splittings from $H^1_{syn}$ and $H^3_{anti}$ is reversed from that given in ref. 21 (see also refs. 20 and 22). [f] The concentration of $H_2C{=}C(Me)CH_2OH$ was 1.2 mol $dm^{-3}$. [g] Because of overlapping lines and the weakness of the spectrum, it was not possible to measure these splitting constants accurately, but they are in the expected range. [h] The concentration of $H_2C{=}CHCH_2OSiMe_3$ was *ca.* 1 mol $dm^{-3}$.

transfer step.[10,11] It has been shown that in aqueous solution the allyloxyl radical is rapidly converted to the hydroxyallyl radical probably without the intermediacy of allyl alcohol, perhaps by the mechanism shown in Scheme 1 thereby avoiding a high-energy transition state of the type **5**.[12]

There is presently considerable interest in oxiranylcarbinyl radicals as sources of allyloxyl radicals and in the chemistry of the latter, because of the potential applications in organic synthesis[13] and in cancer chemotherapy,[14] as well as from the mechanistic standpoint.[1] In principle, the uncatalysed rearrangement of an allyloxyl radical by way of a simple unimolecular 1,2-H-atom shift could be much more rapid than the corresponding rearrangement of the ethoxyl radical, because a stabilised allylic radical is produced in the former reaction thus making it appreciably more exothermic. Hyperconjugative + conjugative delocalisation of the unpaired electron over all four heavy atoms is stereoelectronically feasible in the transition state, and could lower the activation energy for rearrangement relative to a saturated analogue.

Against this background, we have used EPR spectroscopy to investigate the formation and transformation of the oxiranylmethyl, allyloxyl and 1-hydroxyallyl radicals **1**–**3** in nonaqueous media. We have also carried out *ab initio* molecular orbital calculations on the rearrangement of allyloxyl to 1-hydroxyallyl radicals by 1,2-H-atom shift from carbon to oxygen.

## Results and discussion

### Hydrogen-atom abstraction from allyl alcohol

EPR spectroscopy was used to monitor the radicals present during continuous UV irradiation of liquid samples positioned in the microwave cavity of the spectrometer, as described previously.[15] The EPR spectrum of the 1-hydroxyallyl radical **3** was observed during photolysis of a number of precursors of hydrogen-abstracting radicals X$^\bullet$ in the presence of allyl alcohol in cyclopropane solvent [eqn. (2)]. In addition to di-*tert*-butyl peroxide (DTBP), which provides a photochemical source of the *tert*-butoxyl radical [eqn. (6; X$^\bullet$ = Bu$^t$O$^\bullet$)],

$$X{-}X \xrightarrow{h\nu} 2X^\bullet \qquad (6)$$

diethyl peroxide, dicumyl peroxide and tetrakis(trimethylsilyl)-hydrazine[16] [X$^\bullet$ = EtO$^\bullet$, $PhMe_2CO^\bullet$ or $(Me_3Si)_2N^\bullet$, respectively] were also used. UV irradiation of acetone affords the excited triplet state (after intersystem crossing), the hydrogen-abstracting ability of which is similar to that of an alkoxyl radical.†

*anti*-isomers of the 1-hydroxyallyl radical **3S** and **3A** were detected; the spectroscopic parameters are given in Table 1 and

† $(CD_3)_2CO$ was used in EPR experiments to avoid overlap of the spectrum of interest with that of $Me_2\dot{C}OH$.

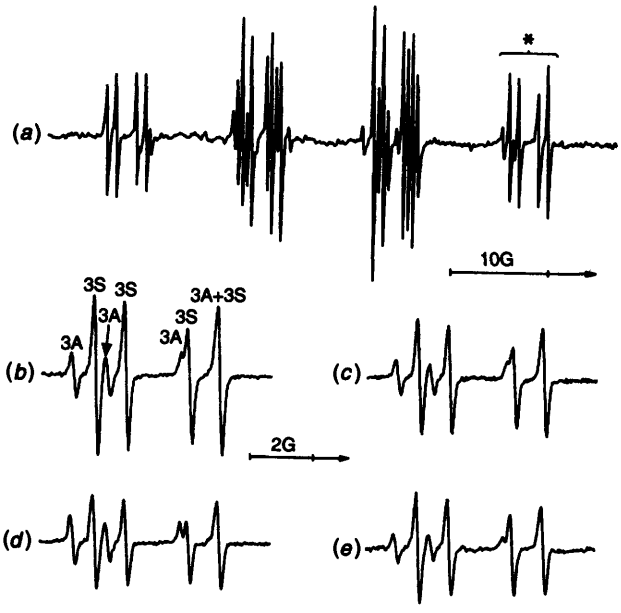
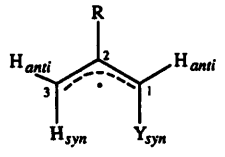
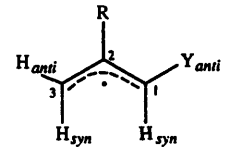



**Fig. 1** EPR spectra of the 1-hydroxyallyl radical (**3S** + **3A**) generated by UV photolysis of various peroxides (each 0.6 mol $dm^{-3}$) in the presence of allyl alcohol (1.2 mol $dm^{-3}$) in cyclopropane at 220 K. The region marked with an asterisk in (*a*) is shown expanded in (*b*)–(*e*): (*a*) and (*b*) from DTBP, (*c*) from dicumyl peroxide, (*d*) from ATBP and (*e*) from diethyl peroxide.




**3S** Y = OH, R = H
**7S** Y = OMe, R = H
**8S** Y = OH, R = Me




**3A** Y = OH, R = H
**7A** Y = OMe, R = H
**8A** Y = OH, R = Me

the assignments of coupling constants follow those established previously for **3** and for other simple allylic radicals.[12,18–22] EPR parameters taken from the literature[20–22] for the 1-methoxyallyl radical **7** and for the 1-hydroxy-2-methylallyl radical **8**, generated in this work by photolysis of DTBP in the presence of 2-methylallyl alcohol, are included in Table 1.

Figs. 1(*a*)–(*c*) and (*e*) show typical EPR spectra obtained during photolysis of three symmetrical peroxides in the presence of allyl alcohol; spectra of the *syn*- and *anti*-isomers of **3** are clearly visible. The isomer ratios were determined by double integration of appropriate lines and were confirmed by computer simulation; the results are given in Table 2. If we assume

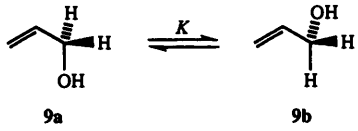
**Table 2** *Syn–anti*-isomer ratios for the 1-hydroxyallyl radical **3** formed by hydrogen-atom abstraction from allyl alcohol in cyclopropane

| Abstracting radical[a] | T/K | [3S]/[3A][b] |
|---|---|---|
| Bu'O' | 180 | 6.69 |
| | 220 | 3.04, 3.17 (1.2), 3.36 (0.6) |
| | 260 | 1.94 |
| EtO' | 180 | 4.26 |
| | 220 | 3.35, 3.65 (1.2), 3.67 (0.6) |
| | 260 | 2.15 |
| $PhMe_2CO^{\bullet}$[c] | 180 | 5.25 |
| | 220 | 3.08 |
| | 260 | 1.88 |
| $(CD_3)_2\dot{C}-O^{\bullet}$ | 180 | 6.19 |
| | 220 | 3.11 |
| | 260 | 2.13 |
| $(Me_3Si)_2N^{\bullet}$[c] | 180 | 7.10 |
| | 220 | 3.17 |
| | 260 | 2.03 |

[a] The concentration of radical precursor was *ca.* 0.6 mol $dm^{-3}$, unless stated otherwise. [b] The concentration of allyl alcohol was 2.4 mol $dm^3$ unless stated otherwise in parentheses. [c] Concentration of radical precursor was *ca.* 0.2 mol $dm^{-3}$.

that **3S** and **3A** are removed by diffusion-controlled radical–radical reactions which have equal rate constants,[23] then the relative steady-state concentrations **3S** and **3A** will be proportional to the relative rates of their formation, provided that the *syn*- and *anti*-isomers do not interconvert within their lifetimes (*ca.* 1 ms) under the experimental conditions. The barriers associated with this type of isomerisation of monosubstituted allyl radicals are relatively large[17,19,21,22] and rotation about the $C^1$–$C^2$ bond in **3** would not be expected to have any measurable effect on the observed value of **[3S]/[3A]** at the temperatures investigated in this work. For example, when the *anti*-isomer of the 1-methoxyallyl radical **7** was generated specifically (by abstraction of hydrogen from *trans*-1-methoxypropene) under conditions similar to those used here, the EPR spectrum of the *syn*-isomer was detectable only above 313 K.[21] Furthermore, as described later, when the 1-hydroxyallyl radical is generated by routes other than hydrogen abstraction from allyl alcohol, different values of **[3S]/[3A]** are found under otherwise similar conditions. Hence, the interconversion of **3S** and **3A** can be neglected for our purposes.

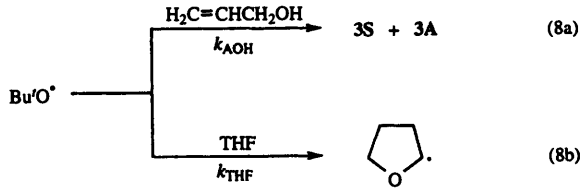
Inspection of Table 2 shows that the value of **[3S]/[3A]** is fairly independent of the nature of the hydrogen-abstracting radical X' and also of the concentration of allyl alcohol; it does, however, increase with decreasing temperature. Spectroscopic measurements[24] and theoretical calculations[25] indicate that two conformations of allyl alcohol need to be considered with respect to rotation about the CH–$CH_2OH$ bond; these are **9a** and **9b**, in which either the C–O bond or a C–H bond eclipses the double bond. In dilute solution in weakly interacting solvents these two conformations are probably about equally populated[24,25] and the barrier separating **9a** and **9b** is sufficiently small (*ca.* 4–8 kJ $mol^{-1}$) that effective equilibrium between them will be maintained under our conditions.




**9a** **9b** (7)

We propose that **9a** reacts with X' to give **3S**, while **9b** gives **3A**, and thus that $[3S]/[3A] = (k_{9a}/k_{9b}K)$, where $K$ is the conformational equilibrium constant and $k_{9a}$ and $k_{9b}$ are the rate constants for abstraction of hydrogen from the two conformations. It is very reasonable that the value of $(k_{9a}/k_{9b})$ at 220 K should be almost the same for all the radicals X' listed in Table 2. All the X–H bonds will be of similar strength, all X' are similarly electrophilic, steric effects should have a negligible influence on the relative reactivities of the two conformations and the activation energies will be relatively small.[26] The temperature dependence of **[3S]/[3A]** will reflect the composite temperature dependences of the rate and equilibrium constants and, for stereoelectronic reasons, we suggest that $k_{9a}$ is larger than $k_{9b}$. Thus, in the conformation **9a** there are two C–H bonds which make a relatively small dihedral angle of 30° with the C-$2p_\pi$ orbitals of the double bond, while in **9b** there is only one such C–H bond; the other is orthogonal to the π-system and allylic delocalisation of the unpaired electron will be available in the transition state for abstraction of hydrogen from this C–H bond only after rotation about the CH–$CH_2OH$ bond in the original alcohol. If $K$ is *ca.* 1,[24,25] then **[3S]/[3A]** should be >1, as observed, and the increase in **[3S]/[3A]** as the temperature decreases probably reflects mainly the lower activation energy for abstraction from **9a** than from **9b**, although changes in $K$ could also contribute.

The reactivity of allyl alcohol (AOH) towards hydrogen abstraction by *tert*-butoxyl radicals was determined in the usual way[15] by competitive reaction with tetrahydrofuran (THF) [eqn. (8)], on the basis that $(k_{AOH}/k_{THF})$ is given by eqn. (9).[15,23]



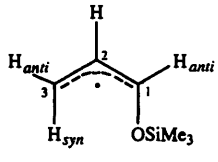

**10**

$$(k_{AOH}/k_{THF}) = \{[3S] + [3A]\}[THF]/[\mathbf{10}][H_2C{=}CHCH_2OH] \quad (9)$$

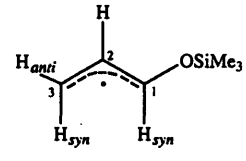
The Arrhenius rate expression for $k_{THF}$ has been determined previously[27] and is given by eqn. (10), where $\theta = 2.303RT$ kJ $mol^{-1}$,

$$\log_{10}(k_{THF}/dm^3\ mol^{-1}\ s^{-1}) = (8.7 \pm 0.8) - (10.5 \pm 4.2)/\theta \quad (10)$$

and THF is very reactive towards Bu'O' ($k_{THF} = 1.6 \times 10^6$ $dm^3$ $mol^{-1}$ $s^{-1}$ at 220 K). However, allyl alcohol is even more reactive and $(k_{AOH}/k_{THF})$ was found to be 1.4 at 220 K, indicating that $k_{AOH}$ is *ca.* $2.3 \times 10^6$ $dm^3$ $mol^{-1}$ $s^{-1}$ at this temperature. The relative rate constants for hydrogen-atom abstraction from 2-methylallyl alcohol to give **8**, from allyloxytrimethylsilane to give **11**, from ethanol to give MeĊHOH and from propan-2-ol to give $Me_2\dot{C}OH$ were determined in similar experiments at 220 K and the rate constants are listed in Table 3.‡ The spectroscopic parameters for **11S** and **11A** are included in Table 1.




**11S**




**11A**

**Experiments with allyl *tert*-butyl peroxide**

Diallyl peroxide has not been characterised adequately[29] and was considered potentially too hazardous to work with. Allyl *tert*-butyl peroxide (ATBP) is readily prepared and comparatively safe to handle;[30,31] it should undergo photolysis to give equal yields of allyloxyl and *tert*-butoxyl radicals [eqn. (11)]

$$H_2C{=}CH{-}CH_2OOBu^t \xrightarrow{h\nu} H_2C{=}CH{-}CH_2O^{\bullet} + Bu^tO^{\bullet} \quad (11)$$

**2**

‡ Hyperfine splittings (in G) at 220 K in cyclopropane: **10**, 13.60 (1H), 27.97 (2H), 2.55 (2H) and 0.75 (2H); MeĊHOH, 15.47 (1H), 22.25 (3H) and 1.06 (O*H*); $Me_2\dot{C}OH$, 19.42 (6H) (the O*H* splitting was not resolved at this temperature).

**Table 3** Relative rate constants ($k_{AOH}/k_{RH}$) in cyclopropane at 220 K for abstraction of hydrogen from RH by *tert*-butoxyl radicals

| RH[a] | $H_2C{=}CHCH_2OH$ (3S + 3A) | $H_2C{=}C(Me)CH_2OH$ (8S + 8A) | $H_2C{=}CHCH_2OSiMe_3$ (11S + 11A) | $MeCH_2OH$ ($MeC\dot{H}OH$) | $Me_2CHOH$ ($Me_2\dot{C}OH$) |
|---|---|---|---|---|---|
| ($k_{AOH}/k_{RH}$) | (1) | 0.97 | 0.91 | 5.4 | 3.4 |
| $k_{RH}$[b]/dm$^3$ mol$^{-1}$ s$^{-1}$ | $2.3 \times 10^6$ | $2.4 \times 10^6$ | $2.5 \times 10^6$ | $4.3 \times 10^5$[c] | $6.8 \times 10^5$[c] |

[a] Radical produced is shown in parentheses. [b] Approximate absolute rate constant, based on $k_{THF} = 1.6 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 220 K. [c] Consistent with data in the literature.[28]

**Table 4** *Syn–anti*-isomer ratios for the 1-hydroxyallyl radical **3** derived from photolysis of allyl *tert*-butyl peroxide in the presence of various alcohols (ROH) in cyclopropane at 220 K

| ROH | [ROH]/mol dm$^{-3}$ | [3S]/[3A][a] |
|---|---|---|
| $H_2C{=}CHCH_2OH$ | 1.2 | 1.63 |
| | 2.4 | 1.70, 1.76[b] |
| $H_2C{=}C(Me)CH_2OH$ | 1.2 | 1.04 |
| | 2.4 | 1.02, 0.97[b] |
| EtOH | 1.2 | 1.05 |
| | 2.4 | 1.04, 1.12[b] |
| PrⁱOH | 1.2 | 1.03 |
| | 2.4 | 1.14 |

[a] The concentration of ATBP was 0.6 mol dm$^{-3}$, unless otherwise stated. [b] [ATBP] = 0.3 mol dm$^{-3}$.

and is likely to be approximately as reactive as allyl alcohol, 2-methylallyl alcohol and allyloxytrimethylsilane towards hydrogen abstraction by alkoxyl radicals.

When ATBP (0.3 or 0.6 mol dm$^{-3}$) was photolysed in the presence of allyl alcohol in cyclopropane solvent, the value of [3S]/[3A] was markedly different from that obtained with the earlier radical sources [see Table 4 and compare Figs. 1(*b*) and (*d*)]; it was also essentially independent of the concentration of allyl alcohol in the range 1.2–2.4 mol dm$^{-3}$. For example, at 220 K the value of [3S]/[3A] obtained with ATBP was 1.7, while the corresponding value obtained using DTBP was 3.0. If we assume equal rates of formation of **3** from the reactions of *tert*-butoxyl and allyloxyl radicals with allyl alcohol, then these results imply that if allyloxyl radicals alone were to be generated in the presence of the alcohol at 220 K, the value of [3S]/[3A] for the resulting 1-hydroxyallyl radicals would be *ca.* 1.0.§

It is very unlikely that the relative rates of formation of **3S** and **3A** by hydrogen abstraction from allyl alcohol by the allyloxyl radical **2** will differ significantly from the rates of their generation by the reactions of other alkoxyl radicals with this alcohol (see Table 2). Thus, it appears that the 1-hydroxyallyl radical **3** is formed from **2** by a route other than direct hydrogen-atom abstraction, presumably one which involves some form of interaction of **2** with the hydroxyl groups of the alcohol, thereby resulting in a formal 1,2-H-atom shift from carbon to oxygen in the alkoxyl radical. The conversion of **2** to **3** by this mechanism must be extremely rapid, because it competes effectively with direct hydrogen-atom abstraction from allyl alcohol by **2**, which should be about as fast as the corresponding abstraction by the *tert*-butoxyl radical ($k_{AOH}$ = *ca.* $2.3 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, see Table 3).

These conclusions are supported by experiments in which ATBP was photolysed in the presence of 2-methylallyl alcohol (MAOH) at 220 K. Thus, when [ATBP] was 0.3 mol dm$^{-3}$ and [MAOH] was 2.4 mol dm$^{-3}$, computer simulation of the EPR spectrum obtained showed that the values of [3]/[8] (0.92) and of [3S]/[3A] (1.03) were both close to unity. This is the expected result if the major fate of Bu'O$^\cdot$ is to abstract hydrogen from MAOH, while the allyloxyl radical interacts with MAOH to bring about a formal 1,2-H-atom shift. Again, the alcohol-induced rearrangement must be very rapid, with a rate constant considerably larger than that for abstraction of hydrogen from MAOH by the allyloxyl radical (*cf.* Table 3).

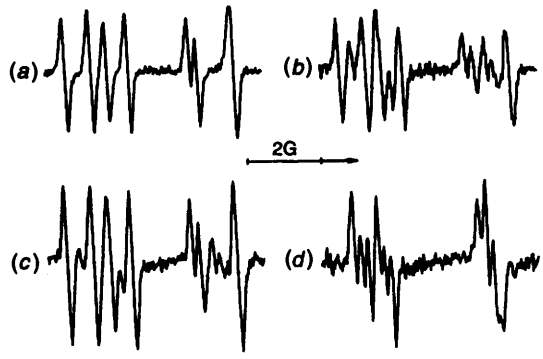



**Fig. 2** Part EPR spectra [region indicated in Fig. 1(*a*)] of **3** and **3-OD** generated during UV irradiation of ATBP in cyclopropane at 220 K in the presence of EtOH and EtOD. (*a*) EtOH (2.4 mol dm$^{-3}$) present. (*b*) EtOD (0.3 mol dm$^{-3}$) present. (*c*) EtOD (3.6 mol dm$^{-3}$) present. (*d*) EtOD (3.6 mol dm$^{-3}$) and $Et_3N$ (0.03 mol dm$^{-3}$) present.

Photolysis of ATBP (0.3 or 0.6 mol dm$^{-3}$) in the presence of ethanol (1.2–2.4 mol dm$^{-3}$) in cyclopropane at 220 K afforded a strong EPR spectrum of the 1-hydroxylallyl radical with [3S]/[3A] = *ca.* 1.0 [see Fig. 2(*a*)]. However, the spectrum of the 1-hydroxyethyl radical was not detectable alongside that of **3**, even when the concentration of ethanol was eight times that of ATBP and thus some $MeC\dot{H}OH$ should be formed by reaction of Bu'O$^\cdot$ with ethanol (see Table 3). We propose that competitive abstraction of hydrogen from ATBP leads to the formation of some acrolein [eqns. (12) and (13)], to which $MeC\dot{H}OH$

$$Bu'O^\cdot + H_2C{=}CH{-}CH_2OOBu' \longrightarrow Bu'OH + H_2C{=}CH{-}\dot{C}HOOBu' \quad (12)$$

$$H_2C{=}CH{-}\dot{C}HOOBu' \longrightarrow H_2C{=}CH{-}CHO + Bu'O^\cdot \quad (13)$$

will add very efficiently to give an α-acylalkyl radical whose EPR spectrum is complex and therefore difficult to detect. Some broad lines which could reasonably be assigned to such adduct radicals were detected under forcing instrumental conditions. Because of its high reactivity towards nucleophilic radicals, only a small steady-state concentration of acrolein would be required to render $MeC\dot{H}OH$ undetectable.¶ Similar results were obtained from the photolysis of ATBP in the presence of propan-2-ol and the spectrum of $Me_2\dot{C}OH$ was not detected alongside that of **3**. Because of the absence of an asymmetric γ-carbon atom, the spectrum of the acrolein adduct $Me_2C(OH)CH_2\dot{C}(H)CHO$ would be expected to be simpler than that derived from addition of $MeC\dot{H}OH$, although two rotamers could still be present because of the slow rotation about the $\dot{C}$–CHO bond typical of such radicals. A broad-lined EPR spectrum ($g$ = 2.0047), analysed on the basis of hyperfine

§ If the values of [3S]/[3A] deriving from the reactions of *tert*-butoxyl and allyloxyl radicals are *a* and *b*, respectively, and the value obtained using ATBP as the primary radical source is *c*, then $b = \{(a + 1)(c + 1)/[2(a + 1) - (c + 1)]\} - 1$.

¶ The β-scission reaction (13) may not be very rapid because, if it were, the consequent chain decomposition of ATBP would lead to a marked dependence of the EPR spectrum on the extent of UV irradiation, which was not observed.

splittings of 18.2 ($2H_\beta$), 17.3 ($1H_\alpha$) and 1.24 G (C*H*O), was detected and an indistinguishable spectrum was observed when $Me_2CHOD$ was used in place of propan-2-ol (see below). These spectroscopic parameters are in accord with the proposed assignment and, in particular, the splitting of 1.24 G attributed to the aldehydic proton is similar to that reported for radicals of related structure.[4,32] However, the lines corresponding to $M_I(2H_\beta) = 0$ were broadened so as to render them undetectable at 220 K, presumably because of exchange of instantaneously nonequivalent β-protons, at an intermediate rate on the EPR timescale, as a result of restriction of rotation about the $C_\alpha$–$C_\beta$ bond. Attempts to generate the same adduct radical by UV irradiation of solutions containing DTBP, propan-2-ol and low concentrations of acrolein were hampered by the formation of insoluble (presumably) polymeric products which evidently contained trapped radicals. Nevertheless, EPR spectra were observed which were essentially identical to those obtained in the experiments with ATBP. When the more reactive allyl or 2-methylallyl alcohol is present in place of ethanol or propan-2-ol, there should be less attack of Bu$^t$O$^\bullet$ on the ATBP and the stabilised 1-hydroxyallylic radicals derived from the former alcohols would be expected to add relatively slowly to acrolein. This accounts for the fact that **3** and **8** are detectable when ATBP is photolysed in the presence of allyl alcohol and 2-methylallyl alcohol, respectively.

Support for this interpretation was obtained from experiments using allyloxytrimethylsilane (ATS), which is also more reactive than ethanol or propan-2-ol towards hydrogen-atom abstraction by Bu$^t$O$^\bullet$ (Table 3). When ATBP was photolysed in the presence of both ethanol and ATS, the EPR spectrum of the allylic radical **11** was observed alongside that of **3**. When [ATS]/[ATBP] was 5, computer simulation of the overlapping spectra showed that **[3]/[11]** was 1.1, while **[3S]/[3A]** was still *ca.* 1.0. This result indicates that Bu$^t$O$^\bullet$ now abstracts hydrogen mainly from ATS, while the allyloxyl radical **2** undergoes an ethanol-induced conversion to **3**.

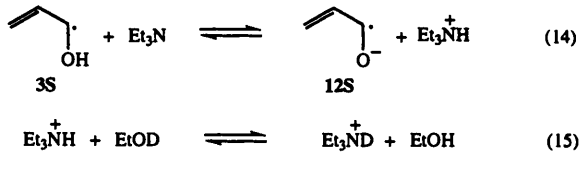
We conclude that alcohols in general induce the formal rearrangement of the allyloxyl radical **2** to give the 1-hydroxyallyl radical **3** such that the isomer ratio **[3S]/[3A]** is close to unity at 220 K, a value appreciably different from that (*ca.* 3) which results when **3** is generated by hydrogen-atom abstraction from allyl alcohol.

### Deuterium labelling experiments

For reference purposes, partially *O*-deuteriated **3** was generated by photolysis of DTBP in the presence of partially *O*-deuteriated allyl alcohol (*ca.* 1.2 mol dm$^{-3}$, prepared by exchange of the normal alcohol with $D_2O$). The values of $a$(OD) (0.17 G for **3S-*O*D** and 0.21 G for **3A-*O*D**) are in accord with expectation, presumably negative in sign and therefore slightly larger in magnitude than $(\gamma_D/\gamma_H) \times a$(OH) for **3**. Computer simulation of the spectrum obtained at 220 K showed that **[3S-*O*D]/[3A-*O*D] = [3S]/[3A] = 3.1**.

UV irradiation of a cyclopropane solution containing ATBP (0.6 mol dm$^{-3}$) and EtOD (99+ atom% D, 0.3 mol dm$^{-3}$) afforded the part-spectrum shown in Fig. 2(*b*) and a similar spectrum was observed with half this concentration of ATBP. Both **3** and **3-*O*D** are present and the composite spectrum could be computer simulated with **[3-*O*D]/[3] = 0.59** and **[3S]/[3A] = [3S-*O*D]/[3A-*O*D] = 1.04**. However, as the concentration of EtOD was increased the extent of deuterium incorporation into **3** passed through a maximum and then decreased, as is evident from comparisons of Fig. 2(*b*) and (*c*). The latter spectrum was obtained when [EtOD] was 3.6 mol dm$^{-3}$ and corresponds to **[3-*O*D]/[3] = 0.38**, while the *syn*:*anti* isomer ratio remained unchanged at *ca.* 1:1. The variation of **[3-*O*D]/[3]** as a function of the concentration of EtOD is given in Table 5 and is shown graphically in Fig. 3. This unexpected result implies that the 1-hydroxyallyl radical does not undergo H/D exchange with EtOD within the lifetime of the radical under the experimental conditions (*ca.* 1 ms) and also indicates that there are (at least) two mechanisms for the conversion of **2** to **3** in the presence of ethanol, one that results in incorporation of deuterium from EtOD and one that does not, when presumably the hydroxyl hydrogen atom in **3** originates from the $CH_2$–O$^\bullet$ group of **2**. The concentrations of **3-*O*D** and **3** are approximately equal when [EtOD] is in the range 1–2 mol dm$^{-3}$, but the *O*-protiated radical dominates at either very high or very low concentrations of EtOD.

Addition of a small amount of triethylamine dramatically increases the extent of deuterium incorporation into **3**. This is clearly evident from comparison of Fig. 2(*c*) and (*d*), where the latter was obtained from a sample in which [EtOD] was 3.6 mol dm$^{-3}$ and [$Et_3N$] was 0.03 mol dm$^{-3}$. We attribute this effect of the amine to its catalysis of H/D exchange of **3** with EtOD, when reactions (14) and (15) both take place rapidly




within the lifetime of **3**, but still slowly on the EPR timescale. Conformational equilibration of the acrolein radical anions **12S** and **12A** would not be expected to occur within their lifetimes and thus the *syn*:*anti* composition of **3** should be unaffected by the base-catalysed exchange process, as observed.

**Table 5** Isomeric and isotopic composition of **3** formed by photolysis of ATBP in the presence of EtOD in cyclopropane at 220 K[a]

| [EtOD]/mol dm$^{-3}$ | [3-*O*D]/[3] | [3S]/[3A] | [3S-*O*D]/[3A-*O*D] |
|---|---|---|---|
| 0.3 | 0.59 | 1.09 | *b* |
| 0.6 | 0.99 | 0.99 | *b* |
| 1.2 | 1.03 | 1.02 | *b* |
| 1.8 | 0.96 | 0.98 | *b* |
| 2.4 | 0.61 | 1.00 | *b* |
| 3.6 | 0.38 | 0.98 | *b* |
| 3.6[c] | *ca.* 40 | *b* | 1.04 |

[a] The concentration of ATBP was 0.6 mol dm$^{-3}$; when it was 0.3 mol dm$^{-3}$ the results were very similar. [b] The *syn*:*anti* ratio was difficult to measure accurately, but was *ca.* 1:1. [c] Triethylamine (0.03 mol dm$^{-3}$) was also present; the EPR spectrum was essentially unchanged when the concentration of the amine was doubled.

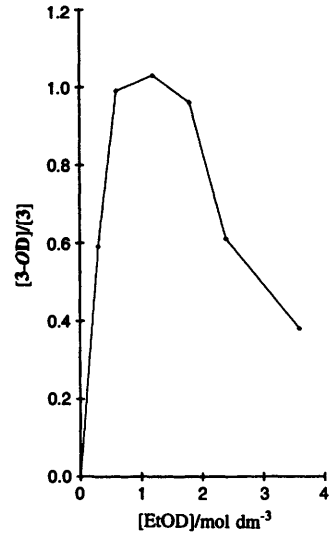



**Fig. 3** Graph showing the variation of **[3-*O*D]/[3]** as a function of [EtOD] during photolysis of ATBP (0.6 ml dm$^{-3}$) in the presence of the deuteriated alcohol at 220 K.

### Experiments with epibromohydrin and epichlorohydrin

In previous work[3,4] the 1-hydroxyallyl radical **3** was detected during UV irradiation of solutions containing DTBP, triethylsilane and epibromohydrin. Under these conditions the oxiranylmethyl radical **1**, generated by reactions (16) and (17),

$$Bu^tO^{\bullet} + Et_3SiH \longrightarrow Bu^tOH + Et_3Si^{\bullet} \quad (16)$$

$$Et_3Si^{\bullet} + BrCH_2{-}CH(O){-}CH_2 \longrightarrow Et_3SiBr + H_2\dot{C}{-}CH(O){-}CH_2 \quad (17)$$

$$H_2C{=}CH{-}CH_2O^{\bullet} + Et_3SiH \longrightarrow H_2C{=}CH{-}CH_2OH + Et_3Si^{\bullet} \quad (18)$$

undergoes rapid ring opening to give the allyloxyl radical **2** [reaction (1)]. The 1-hydroxyallyl radical was believed to be produced by hydrogen-atom abstraction from allyl alcohol, formed by hydrogen transfer to **2**.[3,4] If triethylsilane were the source of hydrogen [reaction (18)], a chain reaction should ensue, leading to rapid consumption of the epibromohydrin.

However, when this experiment was repeated the isomeric composition of **3** ([**3S**]/[**3A**] = 1.05 at 220 K) indicates that it is formed by the alcohol-induced rearrangement of **2**, rather than by hydrogen abstraction from allyl alcohol [see Fig. 4(*a*)].

*tert*-Butoxyl radicals abstract hydrogen from trimethylamine–butylborane (TMBB) much more rapidly than from triethylsilane and the trimethylamine–butylboryl radical **13** so formed [reaction (19)] is an excellent reagent for the abstraction

$$Bu^tO^{\bullet} + Me_3N{\rightarrow}BH_2Bu \longrightarrow Bu^tOH + Me_3N{\rightarrow}\dot{B}HBu \quad (19)$$

**13**

$$Me_3N{\rightarrow}\dot{B}HBu + ClCH_2{-}CH(O){-}CH_2 \longrightarrow Me_3N{\rightarrow}BH(Cl)Bu + H_2\dot{C}{-}CH(O){-}CH_2 \quad (20)$$

of bromine or chlorine from alkyl halides.[33] UV irradiation of a cyclopropane solution containing DTBP, TMBB and epichlorohydrin (each 0.6 mol dm$^{-3}$) at 220 K afforded an EPR spectrum which was very similar to that shown in Fig. 4(*a*). Now the oxiranylmethyl radical **1** is generated by reaction (20)[33] and, again, the isomeric composition of **3** indicates that it is formed by the alcohol-induced rearrangement of **2**. The chloroborane complex produced in reaction (20) is much less reactive towards nucleophiles than is $Et_3SiBr$ and the high reactivity of TMBB towards $Bu^tO^{\bullet}$ means that competitive abstraction of hydrogen from added alcohols can be kept to a minimum. Figs. 4(*b*) and (*c*) show part-spectra of **3** generated by the epichlorohydrin/TMBB route in the presence of allyl alcohol (1.2 mol dm$^{-3}$) and ethanol (1.2 mol dm$^{-3}$), respectively. With allyl alcohol, the value of [**3S**]/[**3A**] is 1.18, slightly larger than that (1.01) obtained with ethanol, presumably reflecting a small amount of hydrogen abstraction from the allyl alcohol by *tert*-butoxyl radicals to give **3**. Similar EPR spectra were obtained with propan-2-ol and with 2-methylallyl alcohol and the results are summarised in Table 6. With 2-methylallyl alcohol the value of [**3S**]/[**3A**] was 0.96 and a weak spectrum of the 1-hydroxy-2-methylallyl radical **8** was also detected, confirming the interpretation of the result obtained using allyl alcohol. The experiments with epichlorohydrin thus support the conclusions from the work with ATBP and also confirm that the acrolein generated in the latter experiments does not influence the formation of **3**.

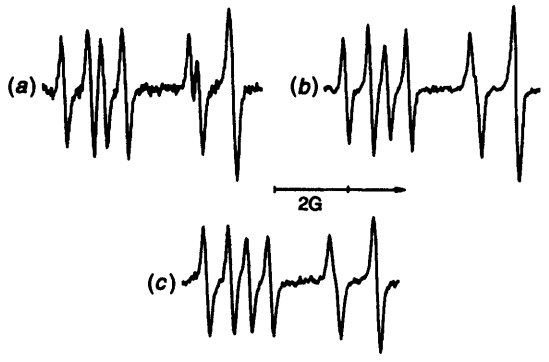



**Fig. 4** Part EPR spectra [region indicated in Fig. 1(*a*)] of **3** generated during UV irradiation of DTBP in cyclopropane at 220 K in the presence of (*a*) $Et_3SiH$ and epibromohydrin, (*b*) TMBB, epichlorohydrin and allyl alcohol (1.2 mol dm$^{-3}$), and (*c*) TMBB, epichlorohydrin and ethanol (1.2 mol dm$^{-3}$). All reagent concentrations were 0.6 mol dm$^{-3}$ unless stated otherwise. Some small differences in the splitting constants, as a function of the medium, are evident.

Using the epichlorohydrin/TMBB route to **2** in the presence of EtOD (0.36–3.6 mol dm$^{-3}$) gave rise to isomer ratios [**3**–*OD*]/[**3**] which did not vary in the manner shown in Fig. 3, but instead increased steadily as the concentration of EtOD increased. We attribute this difference to the presence of a small amount of trimethylamine or other base, derived from reactions of TMBB, in the samples which leads to exchange of **3** with EtOD (*cf.* before). This was supported by experiments in which ATBP was photolysed in the presence of EtOD and TMBB, when the extent of deuterium incorporation into **3** was much greater than in the absence of the amine-borane.

### Molecular orbital calculations

*Ab initio* calculations were carried out using the GAUSSIAN92 package of programs[34] in conjunction with the standard 6-31G** basis set. Geometries were optimised at the UHF level (RHF level for acrolein) using the gradient method and electron correlation was included in single-point calculations using Møller–Plesset perturbation theory taken to third-order [UMP3(full)/6-31G**//UHF/6-31G** level]. The nature of every stationary point (local minimum or transition state) was confirmed by evaluating the complete set of normal harmonic frequencies, which also allowed computation of the zero-point vibrational energies (ZPVEs). Spin contamination proved to be a problem for some species investigated and annihilation of contaminating quartet states, using the standard procedure included in GAUSSIAN92, afforded energies at the PMP3 level, which have previously proved adequate to describe related systems when considerable spin contamination was present.[35] Inclusion of the ZPVEs, scaled by a factor of 0.90 to account for the overestimation of vibrational frequencies at this level of theory,[36] gives the total energies at 0 K [designated $E_0$(MP3) and $E_0$(PMP3)]. The optimised geometries obtained are shown in Fig. 5 and the energies and values of $\langle S^2 \rangle$ are given in Table 7.

The structures of the four isomers of the 1-hydroxyallyl radical (**3SS**, **3SA**, **3AS** and **3AA**) and of the *s-cis* and *s-trans* forms of acrolein (**15S** and **15A**) were optimised within the constraint of planarity. All other structures were optimised without any geometrical constraints, although the equilibrium structure **2a** of the allyloxyl radical has effective $C_s$ symmetry. The energies of the four isomers of **3** are very similar, with **3SS** marginally the most stable and **3AA** the least. The interconversions of **3SS** with **3SA** and of **3AS** with **3AA**, *via* the transition states **3ATs** and **3STs**, respectively, are associated with computed

**Table 6** Isomeric composition of **3** formed by photolysis of DTBP, TMBB, epichlorohydrin and various alcohols in cyclopropane at 220 K

| Alcohol[a] | None | $H_2C{=}$ $CHCH_2OH$ | $H_2C{=}$ $C(Me)CH_2OH$ | EtOH | $Pr^iOH$ |
|---|---|---|---|---|---|
| [**3S**]/[**3A**] | 1.03 | 1.18 | 0.96[b] | 1.01[c] | 0.97[c] |

[a] The alcohol concentration was 1.2 mol dm$^{-3}$; the concentrations of DTBP, TMBB and epichlorohydrin were each 0.6 mol dm$^{-3}$. [b] A very low concentration of the radical **8** was also detected. [c] A very low concentration of the α-hydroxyalkyl radical derived from the alcohol was also detected when the concentration of the latter was increased to 2.4 mol dm$^{-3}$.

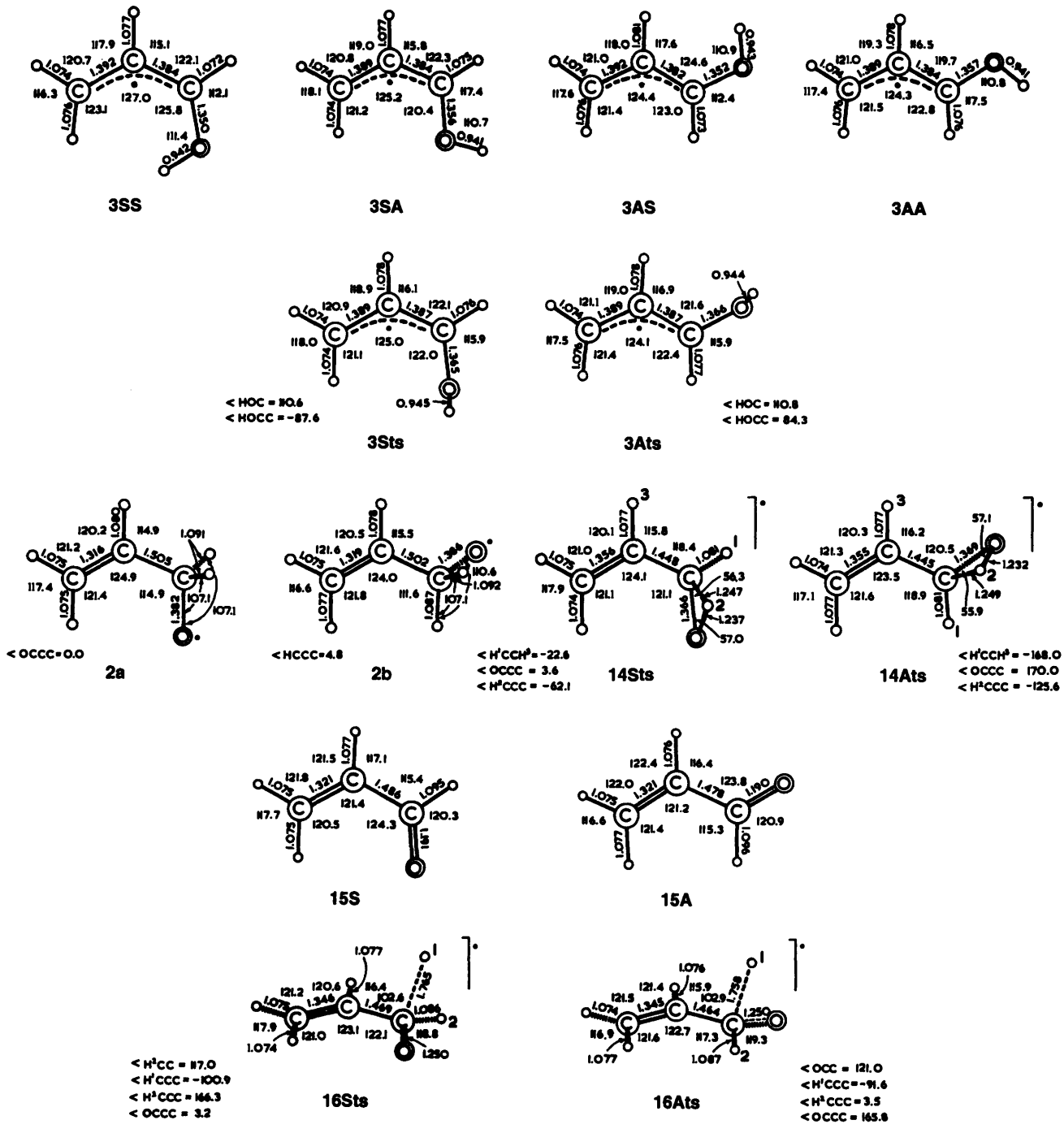



**Fig. 5** Calculated structures for the molecules included in Table 7; bond lengths are in Å, angles are in degrees

barriers of <13 kJ mol$^{-1}$ and it seems very likely that the EPR spectra observed for **3S** and **3A** in the temperature range 180–260 K will be time-averages corresponding to fast exchange by rotation about the C–O bond.

The allyloxyl radical **2** has been investigated previously by Pasto *et al.*[1a,b] using *ab initio* methods and our results are in close agreement with this previous work, although the levels of calculation differ slightly. Two minima were located, structure **2a**, in which the C–O bond lies in the plane of the double bond, and structure **2b** where a C–H bond lies in this plane. These two conformations are analogous to the preferred conformations of allyl alcohol itself (**9a** and **9b**) and, similarly, are predicted to be very close in energy. The allyloxyl radical **2** is calculated to be less stable than the 1-hydroxyallyl radical **3** by *ca.* 93 kJ mol$^{-1}$. The ethoxyl radical ($CH_3CH_2O^{\bullet}$) has been calculated[8] to be less stable by 41 kJ mol$^{-1}$ than the 1-hydroxyethyl radical ($CH_3\dot{C}HOH$) and, since an allylic C–H bond in propene is weaker by 59 kJ mol$^{-1}$ than a C–H bond in ethane,[37] the allylic stabilisation of the radical **3** is reflected in the increased exothermicity of the rearrangement of **2** by 1,2-H-atom shift, as expected.

Two transition structures (**14Sts** and **14Ats**) were located for the intramolecular rearrangement of **2** to **3** and these would presumably lead to **3S** and **3A**, respectively. In fact, at the PMP3 level, β-scission of the allyloxyl radical to give acrolein (**15S** and **15A**) and a hydrogen atom, *via* the transition states **16Sts** and **16Ats**, is marginally more favourable than the 1,2-H-atom shift. However, the key point here is that the predicted activation energy for the unimolecular rearrangement of the allyloxyl radical to the 1-hydroxyallyl radical is very large (*ca.* 111 kJ mol$^{-1}$) and, assuming an *A*-factor of $10^{13}$ s$^{-1}$, would correspond to a rate constant for the 1,2-H-atom shift of $<10^{-13}$ s$^{-1}$ at 220 K, implying that this process will be unobservable. Although the above calculations refer to isolated

**Table 7** Results of molecular orbital calculations using the 6-31G** basis set[a]

| Molecule | $E$(UHF)/ Hartree | $\langle S^2 \rangle$ | $\langle S^2 \rangle$ (annihil.) | ZPVE[b]/ kJ mol$^{-1}$ | $E$[MP3(full)]/ Hartree | $E$[PMP3(full)]/ Hartree | $E_0$(MP3)$_{rel}$/ kJ mol$^{-1}$ | $E_0$(PMP3)$_{rel}$/ kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| **3SS** | −191.334 310 | 0.947 | 0.757 | 198.0 | −191.936 034 | −191.946 220 | 0.0 | 0.0 |
| **3SA** | −191.334 033 | 0.959 | 0.758 | 197.3 | −191.934 547 | −191.945 300 | 3.3 | 1.8 |
| **3AS** | −191.334 147 | 0.954 | 0.757 | 197.6 | −191.935 136 | −191.945 645 | 2.0 | 1.1 |
| **3AA** | −191.333 377 | 0.962 | 0.758 | 196.3 | −191.933 707 | −191.944 576 | 4.6 | 2.8 |
| **3Sts** | −191.331 302 | 0.965 | 0.758 | 195.5 | −191.929 969 | −191.941 055 | 13.7 | 11.4 |
| **3Ats** | −191.330 335 | 0.968 | 0.758 | 194.5 | −191.928 564 | −191.939 787 | 16.5 | 13.8 |
| **14Sts** | −191.240 521 | 1.034 | 0.778 | 184.8 | −191.849 228 | −191.863 755 | 216.0 | 204.6 |
| **14Ats** | −191.240 673 | 1.027 | 0.777 | 184.0 | −191.848 947 | −191.863 270 | 216.1 | 205.2 |
| **2a** | −191.310 551 | 0.761 | 0.750 | 200.7 | −191.910 220 | −191.911 676 | 70.2 | 93.1 |
| **2b** | −191.310 597 | 0.781 | 0.751 | 201.3 | −191.909 009 | −191.911 608 | 73.9 | 93.8 |
| **15S** + H$^{\bullet}$[c] | −191.265 024 | 0.750 | 0.750 | 173.7 | −191.874 768 | −191.874 768 | 139.1 | 165.9 |
| **15A** + H$^{\bullet}$[c] | −191.267 644 | 0.750 | 0.750 | 173.7 | −191.877 177 | −191.877 177 | 132.8 | 159.5 |
| **16Sts** | −191.253 638 | 1.246 | 0.878 | 174.2 | −191.840 316 | −191.863 348 | 229.9 | 196.2 |
| **16Ats** | −191.255 200 | 1.228 | 0.868 | 174.1 | −191.842 161 | −191.864 580 | 225.0 | 192.9 |
| **15S** | −190.766 791 | — | — | 173.7 | −191.376 535 | — | — | — |
| **15A** | −190.769 411 | — | — | 173.7 | −191.378 994 | — | — | — |
| H$^{\bullet}$ | −0.498 233 | 0.750 | — | — | — | — | — | — |

[a] 1 Hartree = 2625.5 kJ mol$^{-1}$. [b] Before scaling. [c] Acrolein and H$^{\bullet}$ separated by 10 Å. Geometry of acrolein as optimised for the isolated molecules (see Fig. 5).

molecules in the gas phase, they do serve as a base from which to develop an understanding of the effects of alcohols on the chemistry of allyloxyl radicals in solution.

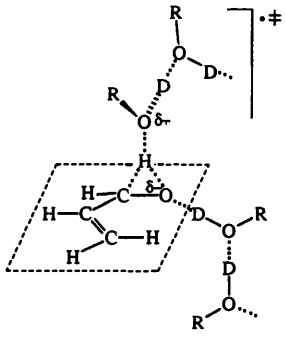
Calculations by Radom and his co-workers[6,38] have indicated that protonation at oxygen in the methoxyl radical lowers the barrier to 1,2-H-atom shift from C to O from 151 to 112 kJ mol$^{-1}$. In general, it appears that 1,2-H-atom shifts in radical cations of the type [HB–ÀH]$^+$ are still associated with relatively high activation energies[38,39] and thus, although it seems probable that the 'partial protonation' associated with hydrogen-bonding of an alcohol molecule to the oxygen atom of the allyloxyl radical may facilitate 1,2-H-atom shift, this effect alone is extremely unlikely to lower the barrier to a point where the rearrangement could take place within the lifetime of the allyloxyl radical (<*ca.* $10^{-6}$ s) in our temperature range.

Hydroxyalkyl radicals $R_2\dot{C}OH$ are known[40,41] to be significantly stronger acids (by *ca.* 4 p$K_a$ units) than the corresponding alcohols $R_2CHOH$, because of the relatively high stability of the radical anion $R_2\dot{C}–O^-$ compared with alkoxide ion $R_2CH–O^-$. It seems likely that the 1-hydroxyallyl radical **3** will be of similar acidity to the 1-hydroxyethyl radical (p$K_a$ = 11.5 in water at 293 K)[40] and the allyloxyl radical should be much more acidic than **3**, because **2** is appreciably less stable than **3**.‖ Hydrogen-bonding to the alkoxyl oxygen atom should act to increase further the acidity of the α-C–H group.

### Mechanism of the formal 1,2-hydrogen-atom shift

A number of mechanistic possibilities exist for the alcohol-promoted rearrangement of the allyloxyl radical to the 1-hydroxyallyl radical. The results of the deuterium-labelling experiments indicate that there are probably two mechanisms for the rearrangement. By one route, hydrogen attached to the oxygen atom in **3** originates from the α-carbon atom of **2**, while by the other pathway the hydroxyl hydrogen originates from the OH/D group of the alcohol.†† There is strong circumstantial evidence that the detailed mechanism of rearrangement depends on the degree of association[42,43] of the alcohol by hydrogen-bonding, small oligomers of the alcohol favouring rearrangement with incorporation of deuterium, while both monomer and large oligomers appear to favour the assisted 1,2-shift of protium.

The relatively high acidity of the α-C–H group in the allyloxyl radical and the probable effect of hydrogen-bonding to oxygen on the rate of rearrangement, discussed above, suggest that a transition state of the type **17** could be involved in the rearrangement without deuterium incorporation, which is dominant at high concentrations of EtOD. At intermediate EtOD concentrations, a mechanism that results in deuterium incorporation into **3** from the OD group of the alcohol becomes of equal importance. Possibly here a specific small oligomer bridges between the α-C–H group and the oxyl oxygen atom to bring about rearrangement with incorporation



**17S**

of deuterium (*cf.* Scheme 1, path B). Different reactivities with respect to carbene insertion into an OH bond have been attributed to different hydrogen-bonded oligomers of methanol and of *tert*-butyl alcohol.[43] A further interesting possibility would be nucleophilic assistance to the 1,2-H shift by the interaction of the alcohol oxygen atom with the C=C bond in the allyloxyl radical (*cf.* $S_N2'$ reactions of allylic compounds). We note that the rearrangement pathways proposed here emphasise the acidity of the α-C–H group of the alkoxyl radical, rather than the basicity of this radical (*cf.* Scheme 1, path A).

The alcohol-induced rearrangement of **2** leads to essentially equal yields of **3S** and **3A** at 220 K, in contrast to hydrogen-atom abstraction from allyl alcohol which gives rise to **3S** as the major product. The rearrangement is clearly a very rapid process and would be expected to be relatively unselective with very similar activation energies for 1,2-H shift *via* the transition state **17S** or its *anti*-analogue **17A**.

‖ Since 1-hydroxyalkyl radicals are in general more stable than the isomeric alkoxyl radicals, the latter will always be more acidic than the former. Therefore, alkoxyl radicals are predicted to be relatively strong carbon acids.

†† Exclusive formation of **3** by the first pathway, followed by partial exchange with EtOD to give **3**–*OD*, is considered much less likely. In this case it would be necessary for the extent of exchange to decrease as the concentration of EtOD increases, which would imply that the rate of H/D exchange decreases appreciably as the degree of association of the alcohol increases.

Finally, we note that simple primary alkoxyl radicals do not undergo alcohol-induced 1,2-H shift as rapidly as the allyloxyl radical, presumably because the product from the former rearrangement (RĊHOH) does not benefit from the allylic stabilisation of **3**. Thus, only EtĊHOH (and no MeĊHOH) was detected during UV irradiation of a cyclopropane solution containing diethyl peroxide (0.6 mol $dm^{-3}$) and propan-1-ol (2.4 mol $dm^{-3}$) at temperatures up to 300 K.

### Inhibition by alcohols of chain reactions involving allyloxyl radicals

The value of [3S]/[3A] determined during UV irradiation of solutions containing DTBP, epihalohydrin and $Et_3SiH$ or TMBB shows that **3** arises almost exclusively from an alcohol-induced formal 1,2-H-shift in the allyloxyl radical. The chain reactions that would otherwise occur in these systems are evidently inhibited in the presence of alcohol, because the allyloxyl radical is rapidly converted to the stabilised 1-hydroxyallyl radical, which is incapable of abstracting hydrogen from the silane or from TMBB. Presumably, a small amount of allyl alcohol‡‡ is rapidly formed at the start of the photolysis and this is then responsible for inhibiting the chain process. When designing chain reactions which involve the intermediacy of primary or secondary allyloxyl radicals,[13] it is thus of crucial importance to recognise the potential effect of alcohols in inducing the rearrangement to the unreactive 1-hydroxyallylic radicals.

## Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz.[15] Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (3 mm i.d., 0.5 mm wall). The light source was a 500 W mercury discharge lamp (Osram HBO 500 W/2) and the optical system has been described.[15] The temperature of the sample during photolysis was determined, using the method described previously;[15a] the heating effect at full light intensity varied between 5 and 7 K depending on conditions.

Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and/or by computer simulation of the composite spectrum. Computer simulations were obtained using a modified version of ESRSPEC2,[44] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

### Materials

Di-*tert*-butyl peroxide (98%, Aldrich) was passed down a column of basic alumina (activity 1) and distilled (bp 46–47 °C/76 Torr); cyclopropane (Union Carbide) and EtOD (Aldrich, nominally 99.5+ atom% D) were used as received. Trimethylamine-butylborane (TMBB) was prepared using a slight modification[15b] of the published procedure.[45] Allyl *tert*-butyl peroxide,[31] tetrakis(trimethylsilyl)hydrazine[16b] and diethyl peroxide[46] were prepared by published methods, although as a precaution diethyl peroxide was purified by trap-to-trap distillation under reduced pressure at room temperature, rather than by distillation at atmospheric pressure as described previously.[46] All other compounds were obtained commercially and purified by standard methods before use if necessary.

‡‡ A still smaller amount of *tert*-butyl alcohol, derived from chain-initiating reactions of *tert*-butoxyl radicals, would also be formed initially.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