Electron Paramagnetic Resonance Spectroscopic Study of the Radicals formed during the Photodecomposition of some Bis(alkenoyl) Peroxides, a Bis(alkynoyl) Peroxide and some Peroxydicarbonates

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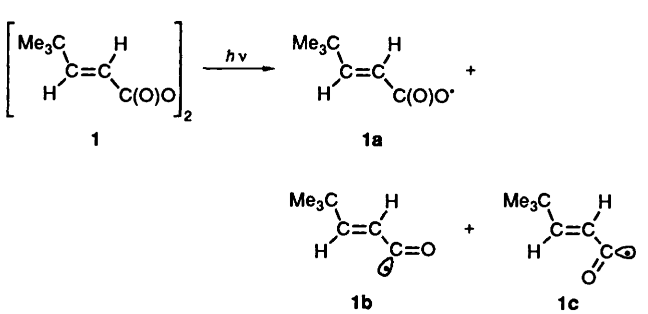
Photolysis, at low temperatures in cyclopropane and/or $CFCl_3$, of bis[(*E*)-4,4-dimethylpent-2-enoyl]-peroxide **1**, bis(4,4-dimethylpent-2-ynoyl) peroxide **2** and dipropyl peroxydicarbonate **3** yielded the corresponding carbonyloxyl radicals, *viz.* $Me_3CCH{=}CHC(O)O^{\bullet}$, $Me_3CC{\equiv}CC(O)O^{\bullet}$ and $PrOC(O)O^{\bullet}$, which were identified by EPR spectroscopy. Carbonyloxyl radicals were not detected on photolysis of bis(3-methylbut-2-enoyl) peroxide **4**, di[(*E*)-cinnamoyl] peroxide **7**, and bis(1-methylpropyl) peroxydicarbonate **9**. All the peroxides also give other radicals many of which were identified from their EPR spectral parameters. Thus, the two bis(alkenoyl) peroxides give the 'corresponding' alkenylacyl radicals, *viz. s-cis-* and *s-trans*-$Me_3CCH{=}CH\dot{C}{=}O$ from **1** and *s-trans*-$Me_2C{=}CH\dot{C}{=}O$ from compound **2**. Evidence is presented which indicates that these acyl radicals may be formed directly during the photolysis of substrates **1** and **4** *via* a Norrish type-1 process. This would represent a new route for the photodecomposition of acyl peroxides with C–O bond scission occurring in competition with the usual O–O bond scission.

The detection of carbonyloxyl radicals, $XC(O)O^{\bullet}$, by electron paramagnetic resonance (EPR) spectroscopy in solution has proven to be surprisingly difficult. The first success was achieved by Yamauchi *et al.*[1,2] who employed laser flash photolysis (LFP) of some diaroyl peroxides to generate the corresponding aroyloxyl radicals, $ArC(O)O^{\bullet}$ [eqn. (1)], which were then detected by time-resolved EPR (TREPR). This procedure has the advantage that it can provide some kinetic data but it suffers from the grave disadvantage that the spectra, which were recorded in the absorption mode, were poorly resolved and showed only a single broad line, $\Delta H_{\frac{1}{2}} = 2.2$–$2.8$ G.[1,2] We have shown that kinetic data on aroyloxyl radicals[3–5] and on other carbonyloxyl radicals[6,7] can be obtained more easily and more reliably by LFP of appropriate peroxide precursors with the time evolution of the radicals being monitored by an absorption they all appear to possess in the visible region of the spectrum. As an outgrowth of our kinetic measurements we calculated that it should be possible, at least in principle, to observe certain classes of carbonyloxyls under the conditions generally employed to obtain well resolved, first-derivative EPR spectra of transient radicals in solution, *viz.*[8] continuous UV irradiation of a solution of the peroxide precursor at low temperatures in the EPR cavity. In the event, our experiments were successful and, in a preliminary communication,[7] we reported that beautiful and well resolved EPR spectra could be obtained for three structurally different carbonyloxyls:[a] (*E*)-$Me_3CCH{=}CHC(O)O^{\bullet}$ **1a**, $Me_3CC{\equiv}CC(O)O^{\bullet}$ **2a** and $PrOC(O)O^{\bullet}$ **3a**. In the present paper we give a full account of our EPR studies on the photolysis of the peroxide precursors of these last three carbonyloxyls and on some structurally related peroxides. Our work with the bis(alkenoyl) peroxides suggests that we may have uncovered a new route for the photodecomposition of acyl peroxides, one which involves a C–O bond scission occurring in competition with the usual O–O bond scission.

$$[ArC(O)O]_2 \xrightarrow{h\nu} ArC(O)O^{\bullet} \qquad (1)$$

Results

1. *Photodecomposition of Bis(alkenoyl) Peroxides.—Bis*[(E)-4,4-*dimethylpent*-2-*enoyl*] *peroxide* **1**. Continuous UV irradiation of this peroxide in cyclopropane or $CFCl_3$ at temperatures 143–173 K gave several radicals and hence gave fairly complex EPR spectra (see Fig. 1*a* and Table 1 for the EPR parameters of the more interesting radicals). Initially, the spectra are dominated by a 2.1 G doublet with *g* 2.0118, which we identify as being due to the carbonyloxyl radical **1a**, and an 18 G doublet, *g* 2.0006, which we identify as being caused by the acyl radical **1b**. A second acyl radical, species **1c**, can also be observed as an asymmetrical, rather broad, 1 G doublet with a similar *g*-value to **1b**. The intensity of the signal due to radical **1c** decreased with increasing temperature and it could not be detected at temperatures > 173 K.



1 **1a** **1b** **1c**

In addition to radicals **1a**, **1b** and **1c** the photolysis of compound **1** yielded a number of other EPR lines (see Fig. 1*a*) which are mostly centred about *g* 2.0023–2.0027. The number of these lines and their intensities and/or line widths varied dramatically with the irradiation time, with the solvent, and with

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[a] We subsequently succeeded in obtaining well resolved EPR spectra for the benzoyloxyl radical and a variety of ring-substituted benzoyloxyls.[9]

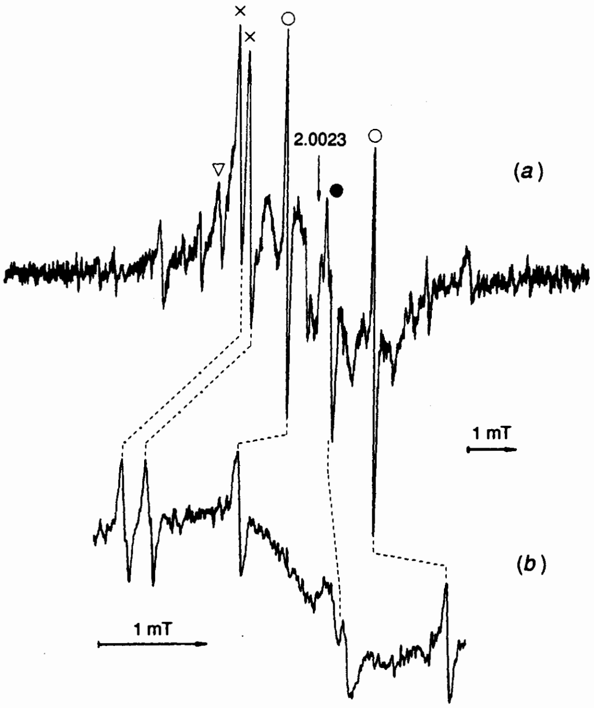
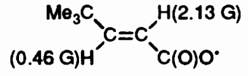


Fig. 1. EPR spectra obtained on photolysis of bis-[(*E*)-4,4-dimethylpent-2-enoyl] peroxide **1** in cyclopropane solution at 147 K (*a*) at 2 mW microwave power level; (*b*) at 10 mW microwave power level, showing alkenoyloxyl radical **1a** (×) and acyl radicals **1b** (○), **1c** (●). The line marked (▽) is tentatively assigned to the acylperoxyl radical **11**.

the initial peroxide concentration.[a] These lines must be due to carbon-centred radicals which do not have an oxygen atom bonded to the radical centre. Since these lines and the lines due to radical **1a** can be 'quenched' by the addition of unsaturated organic compounds, which are known to trap carbonyloxyl radicals, without quenching the signals due to acyl radicals **1b** and **1c** (*vide infra*) it is clear these carbon-centred radicals arise from the attack of species **1a** on the peroxide, the products and the solvent. For this reason, these 'secondary' radicals will not be considered in any detail.[b]

The identification of the different radicals was facilitated by recording of the EPR spectra at various microwave power levels, since the signals assigned to species **1a**, **1b** and **1c** were relatively resistant to power saturation.[c] However, the signals due to the 'secondary' carbon-centred radicals were readily saturated so that simplified spectra could be obtained by working at microwave power levels of 10–50 mW (see Fig. 1*b*). The identification of the radicals was also facilitated by recording the spectra both in the absence and in the presence of oxygen, because carbonyloxyl radicals do not react with molecular oxygen[2–7] whereas all the carbon-centred radicals, including the acyl radicals **1b** and **1c**, are converted into peroxyl radicals at rates which must be close to the diffusion-controlled limit.

The EPR spectrum of the carbonyloxyl radical **1a** can be unequivocally assigned for the following reasons: (i) the *g*-value of 2.0118 is in the range characteristic of carbonyloxyl radicals,[d] (ii) the presence of hyperfine splittings (hfs) due to two different hydrogen atoms ($a^H \sim 2.1$ G and 0.5 G),[d] (iii) the lines due to species **1a** were not eliminated by molecular oxygen, (iv) the lines due to species **1a** were suppressed by the addition of organic compounds such as styrene, toluene and cyclohexa-1,4-diene, compounds which we have shown to be highly reactive towards carbonyloxyl radicals,[3–7] (v) laser flash photolysis of the starting peroxide **1** yielded a transient absorption in the visible spectral region which is similar to the transient absorption found for other carbonyloxyls,[9,16] (vi) the pattern of reactivity (towards organic substrates) of the species responsible for the transient visible absorption is very similar to the pattern of reactivity previously found for the benzoyloxyl radicals,[5,16] (vii) species **1a** could be trapped by olefins[e] and by benzene[f] to give EPR spectra characteristic of carbonyloxyl radical adducts to these compounds. In these last experiments, the EPR signals due to species **1a** and the signals due to the carbon-centred radicals having *g* 2.0023–2.0027 were completely 'quenched' but the signals due to acyl radicals **1b** and **1c** remained very intense in the presence of benzene or toluene, were somewhat reduced in intensity in the presence of (*Z*)-but-2-ene and cyclohexa-1,4-diene, but were completely suppressed only by the highly reactive olefin 1,1-diphenylethylene.



g 2.01176

1a.

The EPR spectrum of the acyl radical **1b** can be assigned with equal certainty as follows: (i) the *g*-value of 2.0006 is in the range characteristic for acyl radicals,[19,20] (ii) the hfs of 18 G due to a single hydrogen is in the range characteristic for 2,3-unsaturated acyl radicals containing a vinylic hydrogen on the 2-carbon and adopting the *s-trans* conformation,[19,20] *i.e.* the conformation in which the hydrogen is eclipsed by the carbonyl group and is antiperiplanar to the SOMO, (iii) the lines due to this radical were suppressed by oxygen, (iv) photolysis of a mixture of di-t-butyl peroxide and (*E*)-4,4-dimethylpent-2-enal in cyclopropane at 153 K gave a radical with an EPR spectrum identical with that of the radical under consideration. This radical can only have the structure **1b**.

The *g*-value of species **1c** identifies this as an acyl radical.[19,20] Its specific identification as the *s-cis* rotamer of **1b** (in which the SOMO and the β-hydrogen are now eclipsed) is based on: (i) the elimination by experiment of acyl radicals of different structure

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[a] For example, in cyclopropane at 153 K a radical is produced with *g* 2.0027, $a^H(1H)$ 22.0 G, 17.5 G and 7.5 G, $a^H(2H)$ 25.5 G. Since this radical is not formed in $CFCl_3$ we can assume that it arises from attack of **1a** on the cyclopropane; a definite structure cannot, however, be assigned.

[b] For carbonyloxyl radicals the signal intensity measured over a range of microwave power 0.1–100 mW had its maximum in the range 18–25 mW.

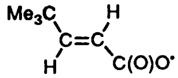
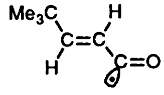
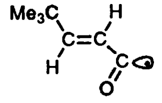
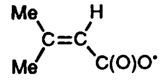
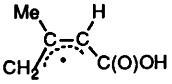
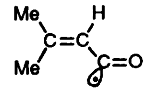
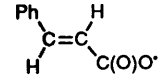
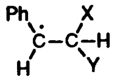
[c] Isotropic *g*-values calculated from crystal data: (*Z*)-ZOC(O)CH=CHC(O)O$^\bullet$, 2.0112 (Z = negative charge), 2.0119 (Z = H, D);[10] (*E*)-ZOC(O)CH=CHC(O)O$^\bullet$, 2.0127 (Z = negative charge), 2.0105 (Z = D);[11] HOC(O)C≡CC(O)O$^\bullet$, 2.0142;[12] PhC(O)O$^\bullet$, 2.0117;[13] $HOC(O)CH_2CH_2C(O)O^\bullet$, 2.009;[14] $CO_3^{\bullet -}$, 2.011.[15] Isotropic *g*-values from solution EPR spectra of benzoyloxyl and ring-substituted benzoyloxyl radicals: 2.0121–2.0125;[2] 2.0109–2.0124.[9]

[d] For comparison, (*Z*)-ZOC(O)CH=CHC(O)O$^\bullet$ (Z = negative charge or H) have an isotropic H hfs of +3.9 G from the nearer vinylic hydrogen.[10] The vinylic H hfs of the corresponding (*E*)-radical are certainly smaller since they could not be resolved.[11]

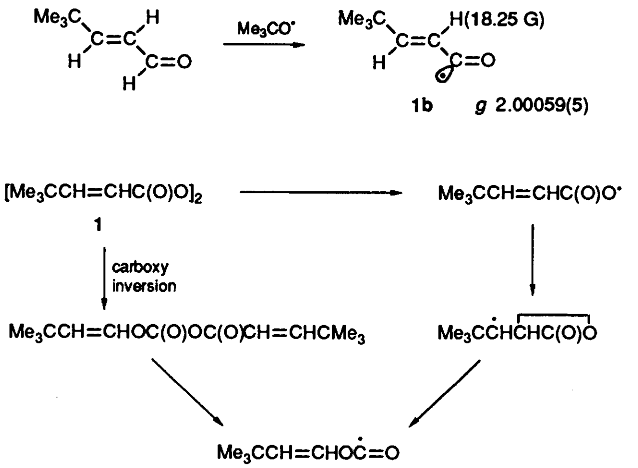
[e] For example, photolysis of compound **1** in the presence of (*Z*)-but-2-ene gave $Me_3CCH{=}CHC(O)OCH(Me)\dot{C}HMe$, *g* 2.002 6(1), $a^H(1H)$ 22.1 G and 16.2 G, $a^H(3H)$ 25.5 G and 0.65 G. These parameters are consistent with those which have been reported for analogous adducts.[17,18]

[f] Photolysis of compound **1** in the presence of benzene gave the cyclohexadienyl radical $Me_3CCH{=}CHC(O)O\dot{C}_6H_6$, *g* 2.002 4(1), $a^H(1H)$ 35.4 G and 13.0 G, $a^H(2H)$ 8.9 G and 2.25 G. These parameters are essentially identical to those obtained by the addition of aroyloxyl[5] and (alkoxycarbonyl)oxyl[6] radicals to benzene.

Table 1. EPR parameters for some of the more important radicals obtained during the photolysis of bis(alkenoyl) peroxides.[a]

(Peroxide)	Radical	Solvent	T/K	g	hfs/G
1	**1a** 	c-C_3H_6 $CFCl_3$	145 158	2.011 76(1) 2.011 8(1)	2.13 (1 H), 0.46 (1 H) 2.10 (1H)
1	**1b** 	c-C_3H_6 c-C_3H_6 $CFCl_3$	153 173 158	2.000 61(3) 2.000 67(5) 2.000 64(8)	18.25 (1 H) 18.03 (1 H) 18.30 (1 H)
1	**1c** 	c-C_3H_6	151	2.000 65(5)	*ca.* 1.0 (1 H)
4	**4a** 			Not detected	
4	**5**[b] 	c-C_3H_6	233	2.003 1(1)	13.40 (3 H), 2.75 (3 H)
4	**6** 	c-C_3H_6	173	2.000 46(5)	18.4 (1 H), 0.40 (3 H)
7	**7a** 			Not detected	
7	**8**[c] 	c-C_3H_6	160	2.003 3(1)	

[a] The EPR parameters for various other radicals are given in the text and in footnotes. [b] This is probably the main radical **5a** but **5b** and/or **5c** are likely to make a contribution (see text). [c] Various benzylic radicals are probably formed (see text).



Scheme 1.

which might, conceivably, be formed during the photolysis of compound **1** and, (ii) the small magnitude of the hfs due to a single hydrogen atom. With regard to (i) we could envisage only two possibilities.

First, an alkoxyacyl radical, $Me_3CCH{=}CHO\dot{C}{=}O$, formed either after a partial, heterolytic 'carboxy inversion'[21,22] of compound **1** and/or by a rearrangement of **1a**, *viz.* Scheme 1. This possibility was eliminated by generation of the unsubstituted vinyloxyacyl radical, $H_2C{=}CHO\dot{C}{=}O$, by abstraction of hydrogen from vinyl formate in cyclopropane at 162 K using photochemically generated t-butoxyl radicals.[a]

$$H_2C{=}CHOCHO \xrightarrow{Me_3CO^{\bullet}} H_2C{=}CHO\dot{C}{=}O$$

$$g\ 2.001\ 05,\ a^{H}(1H)\ 0.75\ G$$

Obviously, the g-value for the vinyloxyacyl radical is significantly larger than the g-value for the radical in question. This relatively high g-value for an acyl radical is in accord with the g-values reported for other alkoxyacyl radicals.[23]

Second, and much less probable, species **1c** might have been a cyclobutylacyl radical derived from a photolytically induced [2 + 2] cycloaddition of the alkenyl moieties of compound **1** followed by further reactions. This possibility can, we believe, be

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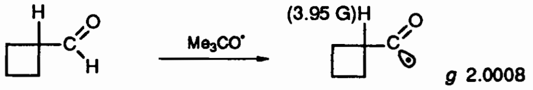
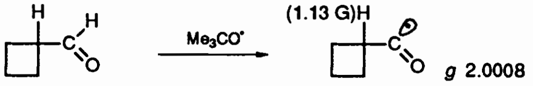
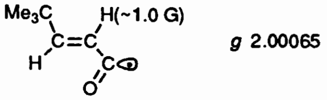
[a] The adduct radical, $Me_3COCH_2\dot{C}HOCHO$, is also produced: g 2.0046, a^H(1H) 16.15 G and 2.35 G, a^H(2H) 13.3 G.

disregarded because hydrogen abstraction from formylcyclobutane by t-butoxyl in cyclopropane at 143 K yielded two rotational isomers of the cyclobutylacyl radical, both of which had higher *g*-values than radical **1c**; the rotamer with the larger hydrogen hfs being formed in a slightly larger amount (ratio *ca.* 1.3 : 1.0).





The small magnitude of the hydrogen hfs for radical **1c** is consistent with the structure assigned.

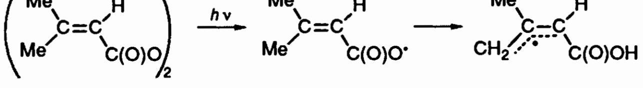


1c

That is, INDO calculations on $H_2C{=}CH\dot{C}{=}O$ give $a^{\mathrm{H}\beta}$ 26.7 G and 0.08 G for this radical in the s-*trans* (≡**1b**) and s-*cis* (≡**1c**) conformations, respectively.[20,a] Furthermore, for acyl radicals which exist in two EPR distinct rotameric forms (*viz.*, cyclopropylacyl,[25,26] oxiranylacyl[26] and carbamoyl[27] radicals) the conformers in which the SOMO and the β-hydrogen are eclipsed have $a^{\mathrm{H}\beta}$-values in the range 0.5–1.6 G, whereas the conformers in which the carbonyl group and the β-hydrogen are eclipsed have $a^{\mathrm{H}\beta}$-values in the range 14–26 G.[b,c]

Bis-(3-methylbut-2-enoyl) peroxide **4**. This peroxide was relatively insoluble both in cyclopropane and in $CFCl_3$ and for this reason solution EPR spectra could only be taken at temperatures >213 K.

Photolysis of a crystallized sample of compound **4** at 148 K yielded a broad quartet centred at *g* 2.0030 and a weak, 18.9 G doublet of fairly sharp lines centred at *g* 2.000 46 [see Figure 2(*a*)]. At temperatures of 213 K and above, where the peroxide was in solution, each line of the broad quartet [a^{H}(3H) 13.4 G] resolved into another quartet with fairly broad lines [a^{H}(3H) 2.75 G, see Table 1]. It is clear that this quartet of quartets must arise from allylic radicals **5** having the general structure $H_2C\cdots\dot{C}(Me)\cdots CHC(O)OR$ with the smaller quartet arising from the methyl group and the larger from the three allylic hydrogens.[30] These radicals are produced predominantly by an intramolecular hydrogen-atom abstraction which yields radical **5a**. This route for the intramolecular decay of the (alkenylcarbonyl)oxyl radical **4a**, *via* a 6-centre, cyclic transition state, has been demonstrated *via* product studies[31,32] and is consistent with the relatively rapid decay of the transient absorption in the visible spectrum which we have observed following LFP of the peroxide **4** and attributed to **4a** (*viz.* lifetimes of 73 ns and 30 ns in CCl_4 and MeCN, respectively, at room temperature).[16]



4 **4a** **5a**

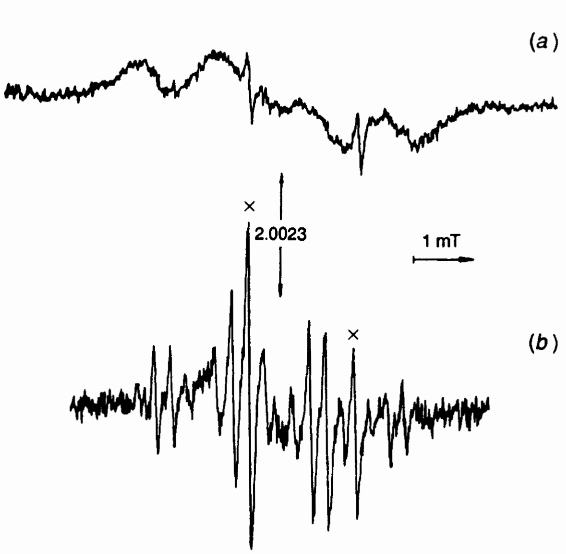
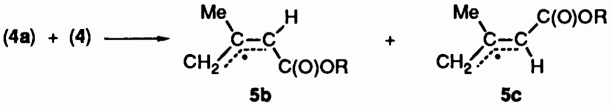


Fig. 2. EPR spectra obtained on photolysis of bis-(3-methylbut-2-enoyl) peroxide, **4**, in (*a*) a frozen cyclopropane solution at 148 K; (*b*) a fluid cyclopropane solution at 233 K. Lines due to acyl radicals **6** are marked by (×).

As mentioned above, even when the EPR spectrum due to radical **5** is fully resolved the lines are still fairly broad and the three different allylic hydrogen atoms are not resolved. This suggests a superimposition of spectra from the structurally related radicals **5b** and/or **5c** formed by intermolecular hydrogen abstraction from the starting peroxide.

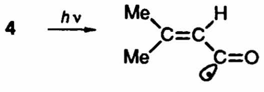


5b **5c**

R = $Me_2C{=}CHC(O)O^-$

Our failure to observe species **4a** by EPR spectroscopy can be attributed to the insolubility of the starting peroxide in cyclopropane and $CFCl_3$, at low temperatures combined with the relatively rapid rearrangement of radical **4a** to **5a**.[16]

The sharp, 18–19 G doublet at *g* 2.000 46 could be observed both in frozen solution at 148 K and in fluid solutions at temperatures 213–273 K [see Fig. 2(*b*)]. The EPR parameters for this radical (see Table 1) identify it as s-*trans*-3-methylbut-2-enoyl **6**. This radical could be identified only in the *s-trans* conformation. However, if this radical is also formed in the *s-cis* conformation in the frozen solution at 148 K it would have



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[a] The hfs by the vinylic hydrogen adjacent to the $\dot{C}{=}O$ moiety shows the same large difference when calculated by Nelsen's method,[24] *viz.* 35.7 G for **1b** and −1.71 G for **1c**.

[b] The rotamer assignment shown for the two cyclobutylacyl radicals is based on these observations.

[c] In this connection we note that for the $Me_2CH\dot{C}{=}O$ radical $a^{\mathrm{H}\beta} \leq 1.5$ G[20,28] but for the sterically much more hindered $(Me_3C)_2CH\dot{C}{=}O$ radical (in which the β-H eclipses the CO group) $a^{\mathrm{H}\beta} \sim 11$ G.[20,29]

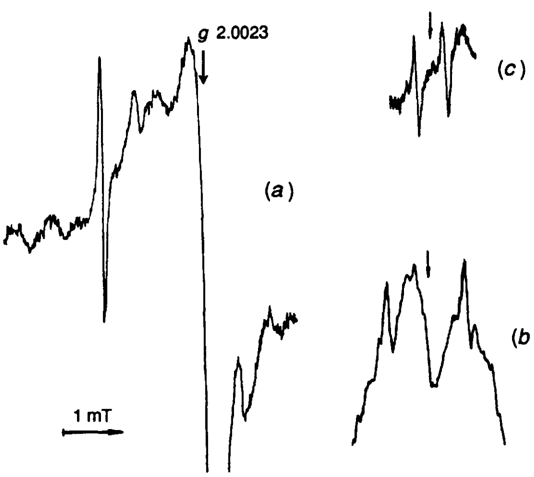
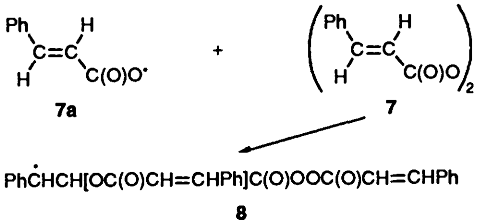


Fig. 3. (*a*) EPR spectrum obtained on photolysis of bis-(4,4-dimethylpent-2-ynoyl) peroxide **2** in $CFCl_3$ solution at 162 K and 2 mW microwave power level; (*b*) region around *g* 2.0126 (arrow) recorded during photolysis of $(Me_3CC{\equiv}^{13}CCO_2)_2$ at 160 K and 50 mW. (*c*) Region around *g* 2.0126 (arrow) recorded during photolysis of $(Me_3CC{\equiv}^{13}CO_2]_2$ at 154 K and 20 mW.

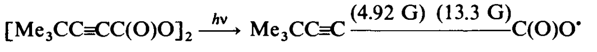
escaped detection because its EPR signal would be masked by one of the broad lines coming from the allyl radicals **5**.

Di-[(E)-*cinnamoyl*] *peroxide* **7**. Photolysis of this peroxide in cyclopropane or $CFCl_3$ solutions at temperatures in the range 150–166 K gave only a very broad (ΔH_{pp} 18–20 G) singlet at $g \sim 2.003$ 3(1) with no trace of the expected (alkenylcarbonyl)oxyl radical **7a** (nor any trace of an alkenylacyl radical). We have previously observed[16] that LFP of compound **7** yields radical **7a** (which can be recognized by the characteristic carbonyloxyl absorption in the visible spectrum). This radical decays fairly quickly and new absorptions 'grow-in' as it decays. These new absorptions could be assigned to benzylic radicals, *e.g.* **8**, formed by the addition of radical **7a** to compound **7**. We therefore attribute the broad singlet at $g \sim 2.0033$ to benzylic radicals such as **8**.



7a **7** **8**

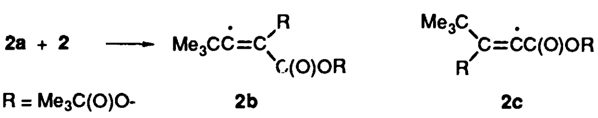
2. *Photodecomposition of Bis-*(4,4-*dimethylpent-*2-*ynoyl*) *Peroxide* **2**.—The EPR spectra obtained during the photolysis of this peroxide at low temperatures depended on whether $CFCl_3$ or cyclopropane was used as the solvent. In $CFCl_3$ the spectra showed three distinctive features (see Fig. 3): (i) a strong, broad ($\Delta H_{pp} \sim 5$ G), asymmetric singlet at $g \approx 2.0030$; (ii) a weak, *ca.* 16 G doublet with *g* 2.0040; and (iii) a sharp singlet at *g* 2.0126. We identify the last mentioned signal as the expected (alkynoyl)oxyl radical **2a** from its characteristic *g*-value, the failure of molecular oxygen to eliminate this signal but its suppression by organic compounds known to be reactive towards carbonyloxyl radicals, and its resistance to microwave power saturation. Final proof was achieved by photolysis of two different ^{13}C-labelled versions of compound **2**, *viz.* $[Me_3CC{\equiv}C^{13}C(O)O]_2$ and $[Me_3CC{\equiv}^{13}CC(O)O]_2$, each of which caused the singlet at *g* 2.0126 to split into a doublet with $a^{13\mathrm{C}}$ 13.3 G and 4.92 G, respectively,[a] (see inserts in Fig.3, and Table 2).



$$[Me_3CC{\equiv}CC(O)O]_2 \xrightarrow{h\nu} Me_3CC{\equiv}C\overset{(4.92\ G)\quad(13.3\ G)}{\overline{\qquad\qquad\qquad}}C(O)O^{\bullet}$$

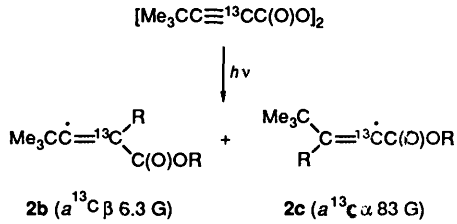
2 **2a** *g* 2.0126

The asymmetry of the strong, broad singlet at *g* 2.0030 suggested that there was a superimposition of EPR signals from two (or more) radicals of generally similar structure. The actual existence of two distinct species could be demonstrated by cutting off the UV irradiation. At 162 K this caused the carbonyloxyl signal due to species **2a** to disappear immediately while one component of the central singlet decayed within one minute to leave a more symmetric, but still broad ($\Delta H_{pp} \sim 4$ G) singlet at *g* 2.0032 which had a lifetime > 1 h at this temperature. This 'two phase' kinetic procedure was observed from 157–313 K. No additional hyperfine splittings could be resolved for the longer lived radical over this temperature range (see Fig. 4*b*). However, at temperatures > 273 K the shorter lived radical showed an incompletely resolved multiplet (see Fig. 4*a*) which must be attributed to the interaction of the unpaired electron with the nine hydrogen atoms of a t-butyl group. On this basis, together with the known facility with which carbonyloxyls add to multiple bonds,[3–7,16] including C≡C triple bonds,[16,34] we can reasonably assign the vinylic structures **2b** and **2c** (which arise from the addition of radical **2a** to its parent peroxide **2**) to the two radicals responsible for the broad singlet.



2b **2c**

Kinetic studies on a wide variety of sterically hindered, persistent vinyl radicals leave no doubt that species **2c** will decay more rapidly than **2b** because it can undergo a rather easy β-scission with loss of a t-butyl radical.[35,36] Indeed, in some experiments the EPR spectrum of $Me_3C^{\bullet}$ [a^{H}(9H) 22.8 G] could be observed. Final confirmation of the position of the radical centre in species **2c** was provided by the magnitude of the ^{13}C hfs obtained on photolysis of $[Me_3CC{\equiv}^{13}CC(O)O]_2$ (see Table 2). The asymmetric singlet was now completely replaced by two broad doublets. The shorter-lived radical had $a^{13\mathrm{C}}$ 83 G, a value typical of a 'bent' (*i.e.*, σ) vinylic radical,[35,37,b] and the longer lived radical had $a^{13\mathrm{C}}$ 6.3 G, a value which seems eminently reasonable for the β-carbon in a vinylic radical.[b] The



2b ($a^{13}C\beta$ 6.3 G) **2c** ($a^{13}C\alpha$ 83 G)

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[a] These measured ^{13}C hfs may be compared with the results of INDO calculations on $HC{\equiv}CC(O)O^{\bullet}$, using the AM1-optimized geometry, which gave $a^{13\mathrm{C}}$ −22.2 G and +16.5 G for $HC{\equiv}C^{13}C(O)O^{\bullet}$ and $HC{\equiv}^{13}CC(O)O^{\bullet}$, respectively, and with experimental values of −13.3 G measured for $Ph^{13}C(O)O^{\bullet}$ in an acetyl benzoyl peroxide single crystal at 35–40 K[33] and −11.3 G measured for $CO_3^{\bullet-}$ in a potassium carbonate single crystal at room temperature.[15]

[b] For $H_2C{=}\dot{C}H$, $a^{13\mathrm{C}\alpha}$ 107.6 G and $a^{13\mathrm{C}\beta}$ 8.6 G; see R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74.

Table 2. EPR parameters for some of the more important radicals obtained during the photolysis of bis-(4,4-dimethylpent-2-ynoyl) peroxide **2** and ^{13}C-labelled **2** in $CFCl_3$.[a]

Radical[b]	T/K	g[c]	hfs/G
2a $Me_3CC{\equiv}CC(O)O^{\bullet}$	162	2.012 6(1)	
$Me_3CC{\equiv}C^{13}C(O)O^{\bullet}$	160	2.012 5(1)	13.3 (^{13}C)
$Me_3CC{\equiv}^{13}CC(O)O^{\bullet}$	155	2.012 64(5)	4.92 (^{13}C)
2b $Me_3C\dot{C}{=}C(R)C(O)OR$	162	2.003 3(2)	
$Me_3C\dot{C}{=}C(R)^{13}C(O)OR$	160	2.003 1(3)	12(1) (^{13}C)
$Me_3C\dot{C}{=}^{13}C(R)C(O)OR$	157	2.002 4(2)	6.3(1) (^{13}C)
2c $Me_3C(R)C{=}\dot{C}C(O)OR$	162	2.002 6(3)	0.75 (9 H at 293 K)
$Me_3C(R)C{=}\dot{C}^{13}C(O)OR$	160	2.002 8(2)	33.6(5) (^{13}C)
$Me_3C(R)C{=}^{13}\dot{C}C(O)OR$	157	2.002 8(2)	83(1) (^{13}C)
2d $Me_3C\dot{C}{=}C(CFCl_2)C(O)OR$	206	2.004 0(3)	16.4(5) (1F)
$Me_3C\dot{C}{=}C(CFCl_2)^{13}C(O)OR$	206	2.003 5(5)	15(1) (1F), 12(1) (^{13}C)
$Me_3C\dot{C}{=}^{13}C(CFCl_2)C(O)OR$	157	2.003 1(5)	15(1) (1F), 28(1)[d] (^{13}C)

[a] See footnote *a*, Table 1. [b] R = $Me_3CC{\equiv}CC(O)^-$. [c] Owing to a superimposition of several radicals having fairly broad lines it proved impossible to obtain more accurate *g*-values. [d] Tentative value, see text and footnotes *e* and *f*.

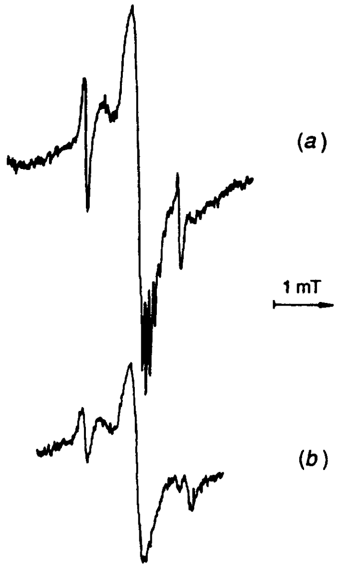
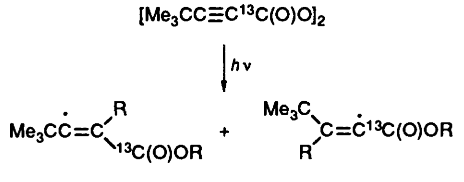


Fig. 4. (*a*) EPR spectrum obtained on photolysis of bis-(2,4-dimethylpent-2-ynoyl) peroxide **2** in $CFCl_3$ solution at 293 K; (*b*) spectrum from (*a*) recorded after cutting off the UV irradiation.

only problem with this assignment are claims that the $H_2C{=}\dot{C}C(O)OH$ radical is a linear (*i.e.*, π) radical.[38,39] However, these claims are based only on the ^1H hfs for radicals generated in solid matrices at low temperatures, the $^{13}C_\alpha$ hfs not having been determined. If the $H_2C{=}\dot{C}C(O)OH$ radical is indeed linear under the experimental conditions employed,[38,39] our present results would suggest that this is due to crystal forces.[a] Certainly, a $^{13}C_\alpha$ hfs of 83 G in a vinylic radical must be due to the α-carbon atom in a σ-structure (*i.e.*, **2c**) while a $^{13}C_\alpha$ hfs of 6.3 G can only arise from a more remote carbon atom—which in this case must be the vinylic β-carbon (*i.e.* **2b**).

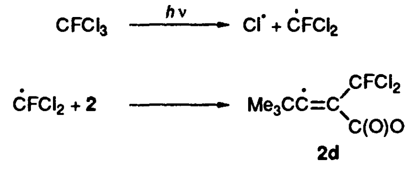
Photolysis of the other ^{13}C-labelled peroxide gave species **2b** and **2c** with the ^{13}C hfs given in Table 2.



2b ($a^{^{13}C}\gamma$ 12 G) **2c** ($a^{^{13}C}\beta$ 33.6 G)

The partial resolution of the ^1H hfs ($a^H \sim 0.75$ G) of the t-butyl group of species **2c** at higher temperatures is consistent with the larger hfs commonly found for a given substituent in the β-position, relative to the α-position, of a vinyl radicals.[37,b] The difference in *g*-values between species **2b** (which could not be determined with precision) and species **2c** (see Table 2) is well within the range found for other vinyl radicals.[c]

The radical responsible for the *ca.* 16 G doublet which was observed on photolysis of compound **2** in $CFCl_3$ was also persistent since it could be detected at 163 K for more than 15 min after cut-off of the UV irradiation. Since we could think of no radical derived solely from compound **2** which would have a 16 G doublet we were forced to assume that the solvent must also be involved. This assumption was supported by the absence of this radical when compound **2** was photolysed in cyclopropane (*vide infra*). We therefore considered a photolytic cleavage of the solvent[d] followed by addition of the $\dot{C}FCl_2$ radical to the precursor peroxide to yield the vinyl radical **2d** with the 16 G hfs arising from the unique fluorine atom.[e] Support for a vinyl radical structure was again provided by the magnitude of the ^{13}C hfs when the ^{13}C-labelled peroxides were photolysed in $CFCl_3$, *viz.* 12 G for the γ-carbonyl carbon atom



R = $Me_3CC{\equiv}CC(O)O$-

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[a] The only linear vinylic π-radical for which a $^{13}C_\alpha$ hfs has been determined (in solution) is $(Me_3Si)_2C{=}\dot{C}SiMe_3$ for which $a^{^{13}C_\alpha}$ 28.1 G.[35]

[b] Furthermore, it allows the ^1H hfs of 0.70 G and 0.67 G in $Me_3C\dot{C}{=}C(Bu^t)OCF_3$ and $Me_3C\dot{C}{=}C(Bu^t)CF_3$, respectively,[35] now to be assigned to the β-t-butyl group.

[c] *e.g.*,[35] $Me_3Si\dot{C}{=}C(H)SiMe_3$, $g = 2.0023$; $Me_3Si\dot{C}{=}C(H)CCl_3$, g 2.0037.

[d] *Note added in proof.* This cleavage is probably not a direct photolytical process but more likely sensitized by excited carbonyl compounds (H. Fischer, personal communication); see also S. A. Davis, B. C. Gilbert, D. Griller and A. S. Nazran, *J. Org. Chem.*, 1984, **49**, 3415.

[e] For comparison,[35] a^F(3F) 4.6, 6.8 and 12.4 G in $Me_3C\dot{C}{=}C(Bu^t)CF_3$, $Me_3C\dot{C}{=}C(Bu^t)OCF_3$ and $Me_3Si\dot{C}{=}C(SiMe_3)OCF_3$, respectively.

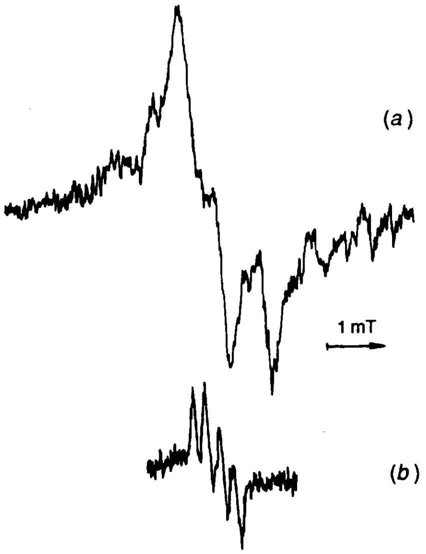
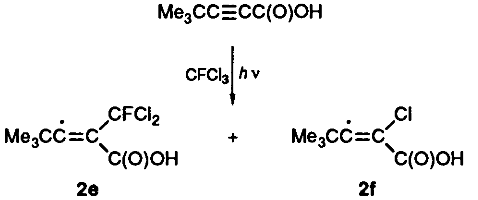


Fig 5. (*a*) EPR spectrum recorded during photolysis of 4,4-dimethylpent-2-ynoic acid in $CFCl_3$ solution at 162 K; (*b*) spectrum obtained from (*a*) at 293 K after cutting off the UV light.

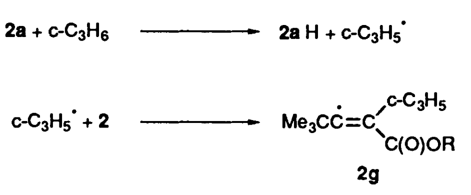
(which is the same as for **2b**) and a tentative[a] value of 28 G for the β-vinylic (or α-vinylic)[b] carbon atom (see Table 2).

Confirmation of the structure **2d** was obtained by photolysis of 4,4-dimethylpentynoic acid in $CFCl_3$. At 164 K the spectrum displayed a 16.3 G doublet with *g* 2.0041, due to species **2e**, and a broad feature at *g* 2.0054 [see Fig. 5(*a*)]. At temperatures above 213 K the latter resolved into a fairly persistent 1 : 1 : 1 : 1 quartet [see Fig. 5(*b*)] clearly due to hfs by a single chlorine atom (a^{35}Cl 2.1 G), *i.e.* species **2f**.



2e **2f**

Photolysis of compound **2** in cyclopropane at 145 K did not yield the carbonyloxyl singlet of **2a** nor the 16 G doublet of **2d**. However, the overlapping broad doublets at *g* 2.0033 due to species **2b** and **2c** *were* formed, plus an additional 9 G doublet with *g* 2.0026 arising from a persistent carbon-centred radical. The absence of radical **2a** in cyclopropane is not entirely surprising since species **2a** is considerably more reactive than (alkenylcarbonyl)oxyl radicals.[16,c] It seems probable that radical **2a** abstracts hydrogen from the cyclopropane solvent and the 9 G doublet is due to the adduct formed between the cyclopropyl radical and compound **2**, *i.e.* species **2g**.



2g

R = $Me_3CC{\equiv}CHC(O)O^-$

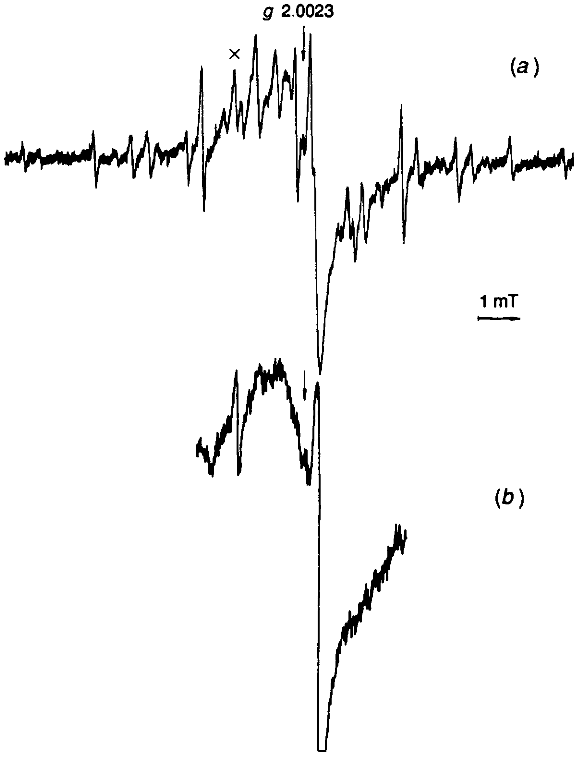


Figure 6. EPR spectra obtained on photolysis of dipropyl peroxydicarbonate in cyclopropane solution at 145 K at microwave power levels of (*a*) 2 mW and (*b*) 50 mW. The hyperfine line of the (alkoxycarbonyl)oxyl radical **3a** is marked by (×).

3. *Photodecomposition of Dialkyl Peroxydicarbonates.—Dipropyl peroxydicarbonate* **3**. Attempts to observe radicals by EPR during the photolysis of this and other dialkyl peroxydicarbonates have been reported by Edge and Kochi.[18b] These workers failed to detect any EPR signals when using cyclopropane as solvent and at temperatures 138–163 K unless olefins were present to act as radical traps. We were, therefore, somewhat surprised to obtain fairly complex, multiline EPR spectra at low (2 mW) microwave power when 5–10% (v/v) solutions of compound **3** were photolysed in cyclopropane at 145 K (see Fig. 6*a*) and in $CFCl_3$ at 162 K. The application of higher microwave power levels (20–50 mW) suppressed most of the EPR lines (see Fig. 6*b*, insert), leaving behind the amplified signals from two singlets at *g* 2.0128 (ΔH_{pp} 0.5 G) and *g* 2.0008 (ΔH_{pp} 1.5 G) (see Table 3).

The radical responsible for the singlet at *g* 2.0128 is obviously the desired (alkoxycarbonyl)oxyl radical **3a**.

$$\underset{\mathbf{3}}{[PrOC(O)O]_2} \xrightarrow{h\nu} \underset{\mathbf{3a}}{PrOC(O)O^\bullet}$$

The radical responsible for the singlet at *g* 2.0008 is equally obviously an alkylacyl radical, most probably the propionyl

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[a] The spectrum of this vinyl radical was poorly resolved and hence the magnitude of the ^{13}C hfs could only be tentatively estimated.

[b] An α-^{13}C hfs of 28 G for this vinylic radical would imply that it is a linear, π-radical" rather than a bent, σ-radical,[35,37] see footnote *b* on the preceding page.

[c] *e.g.*,[16] rate constants for H-atom abstraction from cyclohexane are 2.3×10^7 dm^3 mol^{-1} s^{-1} for **2a** and 7.3×10^5 dm^3 mol^{-1} s^{-1} for (*E*)-PhCH=CHC(O)O•.

Table 3. EPR parameters for some of the more important radicals obtained during the photolysis of dialkyl peroxydicarbonates.[a]

Peroxide	Radical[b]	Solvent	T/K	g	hfs/G
3	**3a** $\mathrm{PrOC(O)O^{\cdot}}$	$CFCl_3$	162	2.012 8(1)	
3	**3b** $\mathrm{Et\dot{C}{=}O}$	$CFCl_3$	162	2.000 8(1)	
3	**3c** $\mathrm{Me\dot{C}HCH_2OC(O)OH}$	c-C_3H_6	155	2.002 7(1)	25.6 (3 H), 22.1 (1 H), 12.7 (2 H)
3	**3d**[c] $\mathrm{Me\dot{C}HCH_2OC(O)OPr}$	$CFCl_3$	162	2.002 6(1)	25.5 (3 H), 22.1 (1 H), 16.9 (2 H)
3	**3e**[c] $\mathrm{Et\dot{C}HOC(O)OPr}$	$CFCl_3$	162	2.002 9(1)	24.0 (2 H), 19.0 (1 H)
9	**9b**/**9c** $\mathrm{Et(Me)\dot{C}OC(O)OR}$	$CFCl_3$	162	2.002 7(1)	21.9 (3 H), 19.6 (2 H)

[a] See footnote *a*, Table 1. [b] R = Et(Me)CHOC(O)O- or H, see text. [c] Photolysis in the presence of dipropyl carbonate.

radical, $\mathrm{Et\dot{C}{=}O}$ **3b**. Certainly this radical cannot be the propoxyacyl radical, $\mathrm{PrO\dot{C}{=}O}$, since such radicals have significantly higher g-values (~2.0011, *vide supra* and ref. 23). The formation of species **3b** is most readily explained by the following reaction sequence.[a] We have also demonstrated, in agreement with this scheme, that in the attack of species **3a** on dipropyl carbonate, abstraction of the α-H is favoured (*vide infra*).

$$\mathbf{3a} + \mathbf{3} \longrightarrow \mathrm{Et\dot{C}HOC(O)OOC(O)OPr} \longrightarrow \mathrm{CO_2} + \mathrm{EtCHO} + \mathbf{3a}$$

$$\mathrm{EtCHO} + \mathbf{3a} \longrightarrow \underset{\mathbf{3b}}{\mathrm{Et\dot{C}{=}O}} + \mathrm{PrOC(O)OH}$$

The major component in the EPR spectra obtained at low levels of microwave power can be assigned to the alkyl radical **3c**. This radical is produced from species **3a** by intramolecular hydrogen-atom abstraction, a reaction which occurs *via* the (normally) favoured, 6-centre, cyclic transition state.

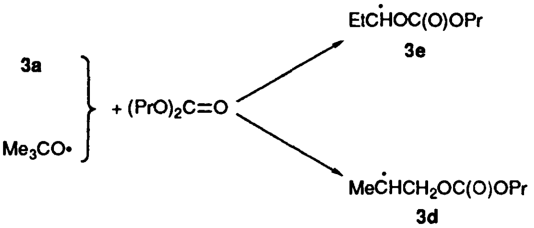
$$\underset{\mathbf{3a}}{\mathrm{PrOC(O)O^{\cdot}}} \longrightarrow \underset{\mathbf{3c}}{\mathrm{Me\dot{C}HCH_2OC(O)OH}}$$

Surprisingly, the two hydrogen atoms of the CH_2 group in alkyl radical **3c** give a hfs of only 12.7 G (see Table 3), a value which is significantly lower than the 16.98 G reported for radical **3d**, which was produced as follows in cyclopropane at 164 K.[18c,b]

$$\mathrm{MeCH{=}CH_2} + \mathbf{3a} \longrightarrow \underset{\mathbf{3d}}{\mathrm{Me\dot{C}HCH_2OC(O)OPr}}$$

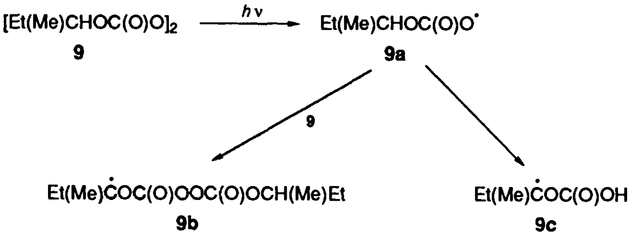
We have confirmed the hfs reported[18c] for alkyl radical **3d** by generating this radical by hydrogen abstraction from dipropyl carbonate. In the presence of an excess of this carbonate, photolysis of compound **3** in $CFCl_3$ at 162 K (or of di-t-butyl peroxide in cyclopropane at 145 K) gave EPR spectra showing the presence of two carbon-centred radicals but no trace of radicals **3a**, **3b** or **3c**. The major component was the α-oxygen-substituted radical **3e**, formed in a reaction essentially identical to that postulated above to account for the formation of propanal and hence of the propanoyl radical. The minor component was species **3d** [$a^{\mathrm{H}}\beta(2\mathrm{H})$ 16.9 G, Table 3]. Despite the unexpected difference in the CH_2 groups' hfs for species **3c** and **3d** we are convinced that the structure of radical **3c** has been correctly assigned. The only other possibility would be the decarboxylated radical product **3f** but this can be ruled out because it is known to have a CH_2 hfs of 23.68 G in cyclopropane at 151 K.[b,41,42]

The value in the hfs of the CH_2 group in radicals structurally related to species **3c**, **3d** and **3f** appears to be largely related to the electron-withdrawing power of the oxygen-linked group,[c] though conformational factors may also play some role. Intra- or inter-molecular hydrogen bonding may affect the magnitude of this hfs for **3c**.



$$\mathbf{3c} \longrightarrow \mathrm{CO_2} + \underset{\mathbf{3f}}{\mathrm{Me\dot{C}HCH_2OH}}$$

Bis-(1*-methylpropyl*) *peroxydicarbonate* **9**. Photolysis of this peroxide in $CFCl_3$ at 162 K gave a fairly intense 12-line EPR spectrum which could be assigned to radical **9b** formed by intermolecular hydrogen abstraction from precursor **9**, or to radical **9c** formed *via* intramolecular hydrogen abstraction involving a 5-centre, cyclic transition state. The experimental



spectrum may actually correspond to a superimposition of the spectrum of both radicals with slightly different hfs, since we failed to simulate the relative line intensities using the hfs given in Table 3.[d] EPR signals arising from neither of the radicals which would be formed in intramolecular hydrogen abstraction *via* a 6-centre, cyclic transition state [*viz.* $\mathrm{Me\dot{C}H(Me)CHOC(O)OH}$ and $\mathrm{Et(\dot{C}H_2)CHOC(O)OH}$] could be identified. If these radicals are present their concentration is less than 20% of the concentration of **9b**/**9c**. The desired carbonyloxyl radical **9a** could not be detected even at microwave power levels of 50 mW.

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[a] The formation of aldehydes in preparatively useful amounts *via* an analogous series of reactions during the thermolysis of t-butyl peroxycarbonates has been demonstrated.[40]

[b] The hfs due to the α-H and the CH_3 group are essentially identical in species **3c**, **3d** and **3f**.

[c] Values reported[42] for CH_2 hfs in some other $\mathrm{Me\dot{C}HCH_2X}$ radicals are: 23.88 G (X = OMe); 17.38 G [X = OC(O)Ph]; and 16.56 G (X = OCF_3).

[d] The unusual line intensity ratios might also be due to selective line broadening arising from restricted rotation of the ethyl group and slightly inequivalent methylene hydrogen atoms.

Discussion

Carbonyloxyl Radicals.—These radicals are not easy to detect by EPR spectroscopy because of their high reactivity towards non-perhalogenated organic compounds (including the peroxides from which they are formed and cyclopropane, the low-temperature solvent most commonly employed in EPR experiments). Fortunately, their resistance to saturation at high microwave power levels has allowed us to detect an (alkenylcarbonyl)oxyl **1a**, an (alkynylcarbonyl)oxyl **2a**, and an (alkoxycarbonyl)oxyl **3a** (as well as seven aroyloxyl radicals).[9] All carbonyloxyl radicals have *g*-values of 2.012 ± 0.001[a] and, in conformity with their generally accepted $^2B_2$ σ-electronic ground state, they show at most only small hfs by neighbouring hydrogen atoms.

Vinyl Radicals.—One of the vinyl radicals produced during the photolysis of $[Me_3CC{\equiv}^{13}CC(O)O]_2$ had a ^{13}C hfs of 83 G (Table 2). Such a large ^{13}C hfs can only arise from an α-carbon in a bent (*i.e.*, σ) vinylic radical. We are reasonably confident that we have correctly identified this radical as $Me_3C(R)C{=}^{13}\dot{C}\text{-}C(O)OR$ **2c** where R = $Me_3CC{\equiv}CC(O)O\text{-}$. As mentioned in the Results section, the problem with this assignment arises because of claims that the $H_2C{=}\dot{C}C(O)OH$ radical is a linear (*i.e.*, π) radical.[38,39] However, these claims are based only on the apparent equivalence of the two vinylic β-hydrogens as determined by EPR spectroscopy on the radical generated in solid matrices at low temperatures. Such apparent magnetic equivalence does not, however, prove that the radical in question is a linear, π-radical rather than a bent, σ-radical. That is, two β-hydrogens in a bent, σ-radical may be 'accidentally' equivalent, or appear so, particularly when the EPR lines are broad as is generally the case for radicals trapped in matrices. Alternatively, the bent radical may invert rapidly on the EPR time-scale so as to make intrinsically non-equivalent β-hydrogens appear equivalent. We have encountered the latter phenomenon with the cyclopropyl[43] and oxiranyl[44] radicals but even for these rapidly inverting radicals the $^{13}C_\alpha$ hfs are large[b] and leave no doubt that they both must be bent σ-radicals. In view of the large $^{13}C_\alpha$ hfs found for the radical that we identify as species **2c** we believe that the conclusion that $H_2C{=}\dot{C}C(O)OH$ is a linear π-radical is certainly open to question.

In this connection, we note that $H_2C{=}\dot{C}C(O)OMe$, $H_2C{=}\dot{C}Ph$ and $H_2C{=}\dot{C}CN$ have also been generated in matrices at low temperatures and, on the basis of magnetically equivalent β-hydrogens, have been described as linear, π-radicals.[37–39,46] Such a structure seems highly probable for $H_2C{=}\dot{C}Ph$ since hfs by the *ortho* and *para* ring hydrogens are also observed[38,39,46] but for the other two radicals the evidence is much less compelling.

A firm decision as to whether any of the above mentioned 'linear' vinyl radicals really are linear π-radicals must await measurements of their $^{13}C_\alpha$ hfs. Such experiments are currently underway.

Acyl Radicals.—The photolysis of the two bis(alkenoyl) peroxides **1** and **4**, led to the formation of the 'corresponding' alkenylacyl radicals, **1b**, **1c** and **6** (see Table 1). Acyl radicals were not detected during the photolysis of dicinnamoyl peroxide **7**, the bis(alkynoyl) peroxide **2**, and (generally) diaroyl peroxides.[47] The acyl radical produced during photolysis of dipropyl peroxydicarbonate **3** is due to propionyl, $Et\dot{C}{=}O$ **3b**, rather than the 'corresponding' propoxyacyl radical $PrO\dot{C}{=}O$. The obvious and important question is: "Does the direct photolysis of bis(alkenoyl) peroxides yield the 'corresponding' acyl radicals **10** *via* a Norrish type-1 process?"

$$[R(R')C{=}CHC(O)O]_2 \xrightarrow[?]{h\nu} \underset{\mathbf{10}}{R(R')C{=}CH\dot{C}{=}O} + \underset{\mathbf{11}}{R(R')C{=}CHC(O)OO^{\bullet}}$$

R = alkyl, R′ = H, alkyl

The alternative is, of course, that these alkenylacyls are 'secondary' radicals formed by the photolysis of some reaction product derived from the (alkenylcarbonyl)oxyl radicals **1a** and **4a**.

The evidence available to answer the above question is somewhat ambiguous. Upon irradiation of a fresh solution of the peroxide the EPR signal due to the acyl radical(s) appears rapidly (within 2 min), though perhaps not 'instantaneously.' The signal intensity grows with time but reaches a steady value within a few minutes. At first sight these result suggest that the acyl radicals are not formed directly from the peroxide. However, the 'delayed' formation of the acyl radicals may also be due to their rapid trapping by trace impurities, particularly by residual traces of oxygen which are likely to be present even after degassing by several freeze–pump–thaw cycles. Only after most of this oxygen has been consumed can the acyl radical's EPR signal 'grow-in.'

The trapping of the acyl radicals with oxygen was demonstrated by photolysis of an oxygen-saturated solution of compound **1** in cyclopropane at 153 K. Under these conditions, only the 2.1 G doublet due to species **1a** and a somewhat asymmetric, broad (*ca.* 3 G) doublet with *g*, 2.0152 appeared immediately upon irradiation. The latter signal is obviously due primarily to peroxyl radicals.[c] A few minutes of continuous irradiation of compound **1** in oxygen-saturated cyclopropane suffices to consume most of the oxygen: the peroxyl signal diminishes in intensity while the signals due to the acyl radicals **1b** and **1c** and the solvent-derived carbon-centred radicals[d] start to 'grow-in.' However, both in this system and in carefully degassed solutions of compound **1** in cyclopropane and in $CFCl_3$ a weak peroxyl radical singlet is always present (*g* 2.0150 and 2.0148, respectively; see Fig. 1) even after prolonged irradiation. If a Norrish type-1 cleavage does occur then this signal may be due to the acylperoxyl radical **11** formed concomitantly with the alkenylacyl radical **10**.

A delayed build-up of a relatively intense EPR signal due to species **1b** which was accompanied by the decay of an initially produced peroxyl radical was also observed during the photolysis of (*E*)-4,4-dimethylpent-2-enoic anhydride in carefully degassed cyclopropane at 153 K.[48] The carbonyloxyl radical **1a** was not observed in this experiment but the 'residual oxygen effect' is the same as that assumed to operate during the photolysis of bis(alkenoyl) peroxides. It therefore lends credence to the view that these peroxides can yield alkenylacyl radicals directly upon photolysis.

The relatively high intensity of the acyl signals produced

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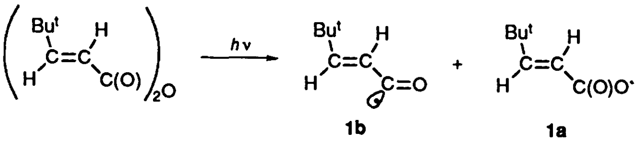
[a] Footnote *b*, p. 1998

[b] For cyclopropyl, $a^{^{13}C_\alpha}$ 95.9 G,[45] for oxiranyl, $a^{^{13}C_\alpha}$ 121 G.[44]

[c] The shape of this signal could be reproduced satisfactorily by a computer simulation by assuming the superimposition of a doublet with a^H 2.9 G (*g* 2.0150), a triplet with $a^H(2H)$ 3.5 G (*g* 2.0147), and the doublet due to radical **1a** in intensity proportions of 1:0.5:0.6. The hfs of the first two radicals agree with the hfs reported for other peroxyl radicals having a single, or two equivalent hydrogens, respectively, on the carbon atom bearing the peroxyl group; see ref. 17, Vol. II/9c2, pp. 8–18; Vol. II/17e, pp. 11–15.

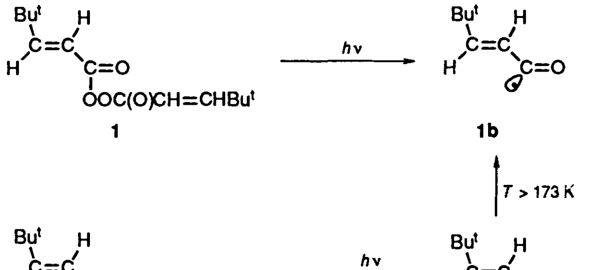
[d] Footnote *b*, p. 1997.



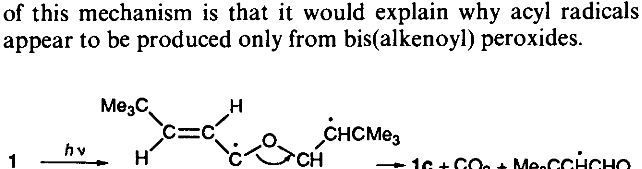
during the photolysis of the bis(alkenoyl) peroxides does not mean that the unsymmetrical cleavage of these molecules is necessarily a major decomposition pathway. The low reactivity of acyl radicals[49] in hydrogen abstractions and additions to multiple bonds compared with carbonyloxyl radicals[3–7,16] causes them to have longer lifetimes and hence to reach higher steady-state concentrations. Indeed, by the addition of benzene or toluene, two compounds which are known to react rapidly with carbonyloxyl radicals[3–7,16] but very slowly with acyl radicals,[49] the EPR signals due to the **1a** radicals could be suppressed completely without influencing the EPR signals due to the 'corresponding' alkenylacyl radicals **1b** and **1c** (see Results section). This fact certainly lends support to the idea that alkenylacyl radicals can indeed be produced by the direct photolysis of bis(alkenoyl) peroxides.

Assuming for the moment that alkenylacyl radicals are directly produced during the photolysis of bis(alkenoyl) peroxides there are two possible reaction mechanisms.

The more probable is a simple bond fission and for compound **1** this could yield both the *s-trans* rotamer **1b** and the *s-cis* rotamer **1c**, depending on the conformation of the peroxide with the *s-cis* radical **1c**, rotating to the more stable *s-trans* form **1b** at temperatures above 173 K on a time-scale comparable to the radicals' lifetimes (*ca.* 10^{-3} s in such experiments).[a]



Alternatively, one can envisage an initial cyclization to produce a 6-membered cyclic 1,4-diradical (as shown below) which then breaks down to yield the *s-cis* radical, CO_2, and a radical most simply formulated as $Me_3C\dot{C}HCHO$. The one advantage of this mechanism is that it would explain why acyl radicals appear to be produced only from bis(alkenoyl) peroxides.



Of course, before attempting to decide between these mechanistic possibilities it is essential whether or not we have uncovered a previously unknown[51] mechanism for the photodecomposition of diacyl peroxides. We believe this can be accomplished by employing time-resolved IR spectroscopy[49,52] by which the growth of the alkenylacyl radical following LFP of the peroxide could be monitored. An 'instantaneous' growth of this IR signal would confirm a direct cleavage, whereas a slow 'grow-in' would indicate an indirect process. Such experiments will be attempted in the near future.

Experimental

Materials.—Dipropyl peroxydicarbonate **3** and bis-(1-methylpropyl) peroxydicarbonate **9** were purchased from Lucidol Penwalt and used as received. Vinyl formate was purchased from Pfaltz & Bauer. Dipropyl carbonate was purchased from Aldrich. All but one of the acyl peroxides were synthesized by the standard procedure described for di[(*E*)-cinnamoyl] peroxide **7**,[53] from the corresponding carboxylic acids[54] *via* their acid chlorides. The latter were prepared by refluxing of the acids with $SOCl_2$ followed by distillation under reduced pressure.[55]

Bis[(E)-4,4-*dimethylpent*-2-*enoyl*] *peroxide* **1**. This was obtained from 4,4-dimethylpent-2-enoic acid[56] *via* 4,4-dimethylpent-2-enoyl chloride[57] (b.p. 68 °C/13 mmHg); white needles, m.p. 68–69 °C; δ_H(CCl_4; $SiMe_4$ int): 7.04 (1 H, d, *J* 16 Hz), 5.70 (1 H, d, *J* 16 Hz) and 1.15 (9 H, s); ν_{max}(CCl_4)/cm^{-1}: 1770s (C=O), 1795vs (C=O), 1645m, 1375m, 1300s, 1095s and 910s.

Bis(4,4-*dimethylpent*-2-*ynoyl*) *peroxide* **2**. To a vigorously stirred solution of 3,3-dimethylbutyne (4.77 g, 0.058 mol) in dry THF (50 cm^3) was added 2.5M butyllithium in hexane (30 cm^3) under nitrogen. After the mixture was cooled to −78 °C, CO_2 was condensed into the solution which was then allowed to warm up to room temperature during 4 h, with CO_2 being bubbled through the solution continuously. The acid was isolated by pouring of the mixture into ice-cold, 10% H_2SO_4 and extraction with diethyl ether. Distillation at 98 °C/8 mmHg afforded white crystals (4.4 g, 60%) of 4,4-dimethylpent-2-ynoic acid, m.p. 48 °C.[58] This was treated with $SOCl_2$[55] to obtain 4,4-dimethylpent-2-ynoyl chloride[58] (b.p. 45 °C/16 mmHg). Reaction of this acid chloride (3.4 g, 0.024 mol) in $CHCl_3$ (10 cm^3) with 20% H_2O_2 (8.2 cm^3, 0.048 mol) and 20% NaOH (4.8 cm^3, 0.024 mol) gave compound **2** (2.3 g, 80%) as white crystals (from pentane), m.p. 60–63 °C; δ_H(CCl_4; $SiMe_4$ int): 1.36s; ν_{max}(CCl_4)/cm^{-1}: 2240vs (C≡C), 1787s, 1763vs (C=O), 1266s, 1140vs and 925 vs.

Bis-(4,4-*dimethyl*[1-^{13}C]*pent*-2-*ynoyl*) *peroxide*. This was prepared from 3,3-dimethylbutyne as described above except for carboxylation with $^{13}CO_2$; m.p. 60–63 °C; δ_H(CCl_4; $SiMe_4$ int): 1.35s; ν_{max}(CCl_4)/cm^{-1}: 2250 and 2230s (sh) (C≡C), 1745s (sh) and 1727vs, (^{13}C=O), 1256s, 1115vs and 925s.

Bis-(4,4-*dimethyl*[2-^{13}C]*pent*-2-*ynoyl*) *peroxide*. This was prepared from commercial $Me_3CC{\equiv}^{13}CH$ (MSD Isotopes) as described above: m.p. 59–62 °C; δ_H(CCl_4; $SiMe_4$ int): 1.36s; ν_{max}(CCl_4)/cm^{-1}: 2220s and 2180s (^{13}C≡C), 1787vs and 1765vs (C=O), 1258s, 1130vs and 923s.

Bis-(3-*methylbut*-2-*enoyl*) *peroxide* **4**. This compound was prepared by a literature procedure[31] with the urea–H_2O_2 complex being used as the oxidizing agent; m.p. 69–71 °C (lit.,[31] 68–69 °C); δ_H($CDCl_3$; $SiMe_4$ int): 5.63 (1 H, m), 2.17 (3 H, d, *J* 2 Hz) and 1.95 (3 H, d, *J* 2 Hz); ν_{max}(CH_2Cl_2) 1777vs (sh) and 1755vs (C=O), 1640vs, 1445s (sh) and 1425s, 1255vs, 1110s, 1045s, 915s and 895s.

Di[(E)-*cinnamoyl*] *peroxide* **7**. This compound was prepared from cinnamic acid: m.p. 138–139 °C (from methanol) (decomp.) (lit.,[53] 132–133 °C); δ_H([$^2H_6$]acetone; $SiMe_4$ int): 7.90 (1 H, d, *J* 16 Hz), 7.4–7.9 (5 H, m) and 6.75 (1 H, d, *J* 16 Hz).

4,4-*Dimethylpent*-2-*enal*. To a solution of 4,4-dimethylpent-2-enoyl chloride (1.33 g, 9.1 mmol) and tetrakis(trihexylphos-

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[a] A somewhat analogous situation was observed during hydrogen-atom abstraction from penta-1,4-diene.[50] At low temperatures both the *E,E* and *E,Z* conformers were obtained, the *E,Z* conformer being converted irreversibly into the *E,E* conformer at *T* > *ca.* 170 K.[50]

phine)palladium (0.11 g, 0.09 mmol) in diethyl ether (10 cm^3) was added tributyltin hydride (2.77 g, 9.5 mmol) during 15 min under N_2.[59] After being stirred for 15 h at room temperature the mixture was treated with a suspension of sodium fluoride (2.5 g) in water (20 cm^3), the mixture was stirred vigorously for 15 min, and the solid precipitate was removed by filtration. The organic phase was separated, washed with water, and the solvent was removed under reduced pressure. Bulb-to-bulb distillation of the residue gave 4,4-dimethylpent-2-enal (0.12 g, 10%), b.p. 60 °C/10 mmHg (lit.,[60] 72–74 °C/50 mmHg); δ_H(CCl_4; $SiMe_4$ int): 9.33 (1 H, d, *J* 7.4 Hz), 6.57 (1 H, d, *J* 16 Hz), 5.84 (1 H, dd, *J*/Hz 16.7and 7.4) and 1.13 (9 H s).

4,4-Dimethylpent-2-enoic anhydride. This was prepared by refluxing of 4,4-dimethylpent-2-enoic acid in acetic anhydride,[61] b.p. 136 °C/10 mmHg; δ_H(CCl_4; $SiMe_4$ int): 6.90 (1 H, d, *J* 15.6 Hz), 5.65 (1 H, d, *J* 15.6 Hz) and 1.20 (9 H, s).

Cyclobutenecarboxaldehyde. This was prepared by oxidation of cyclobutyl methanol with pyridinium chlorochromate[62] (34%); b.p. 108 °C; δ_H(CCl_4; $SiMe_4$ int): 9.47 (1 H, d, *J* 3.0 Hz), 2.7–3.3 (1 H, m) and 1.8–2.4 (6 H, m).

Procedures.—Radicals were generated by direct UV photolysis of samples in the cavity of a Varian E104 EPR spectrometer with the light from a 1000 W high-pressure Hg/Xe lamp. Samples were prepared in 4-mm o.d. quartz tubes, degassed by three freeze–pump–thaw cycles and sealed under vacuum. Trichlorofluoromethane was passed over basic alumina prior to use. ^1H NMR spectra were recorded on a Varian EM360A spectrometer. For the IR spectra, a Perkin-Elmer Model 700 instrument was used. Melting points (uncorrected) were taken on a Fischer Model 355 melting point analyser.

References

1 S. Yamauchi, N. Hirota, S. Takahara, H. Sakuragi and K. Tokumaru, *J. Am. Chem. Soc.*, 1985, **107**, 5021.
2 S. Yamauchi, N. Hirota, S. Takahara, H. Misawa, K. Sawabe, H. Sakuragi and K. Tokumaru, *J. Am. Chem. Soc.*, 1989, **111**, 4402.
3 J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1987, **109**, 897.
4 J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2877.
5 J. Chateauneuf, L. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2866.
6 J. Chateauneuf, J. Lusztyk, B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 6727.
7 H. G. Korth, J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 5929.
8 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 193.
9 H. G. Korth, W. Müller, J. Lusztyk and K. U. Ingold, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 183.
10 M. Iwasaki, B. Eda and K. Toriyama, *J. Am. Chem. Soc.*, 1970, **92**, 3211; K. Toriyama, M. Iwasaki, S. Noda and B. Eda, *J. Am. Chem. Soc.*, 1971, **93**, 6415; B. Eda and M. Iwasaki, *J. Chem. Phys.*, 1971, **55**, 3442.
11 K. Minakata and M. Iwasaki, *J. Chem. Phys.*, 1972, **57**, 4758.
12 H. Muto, K. Toriyama and M. Iwasaki, *J. Chem. Phys.*, 1972, **57**, 3016.
13 N. J. Karch, E. T. Koh, B. L. Whitsel and J. M. McBride, *J. Am. Chem. Soc.*, 1975, **97**, 6729.
14 H. C. Box, H. G. Freund, K. T. Lilga and E. E. Budzinski, *J. Phys. Chem.*, 1970, **74**, 40.
15 G. W. Chantry, A. Horsfield, J. R. Morton and D. H. Whiffen, *Mol. Phys.*, 1962, **5**, 589.
16 H. G. Korth, J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Org. Chem.*, in the press.
17 *Landolt-Börnstein, New Series, Magnetic Properties of Free Radicals*, eds. H. Fischer and K. H. Hellwege, Springer-Verlag, Berlin, 1977 and 1988, Vol. II/9b, pp. 87–89; Vol. II/17b, pp. 126–131.
18 D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, (*a*) 1972, **94**, 7695; (*b*) 1973, **95**, 2635.
19 Reference 17, Vol. II/9b, pp. 318–321; Vol. II/17b, pp. 514–518.
20 A. G. Davies and R. Sutcliffe, *J. Chem. Soc., Perkin Trans. 2*, 1980, 819.
21 S. Oae and K. Fujimori in *The Chemistry of Peroxides*, ed. S. Patai, Wiley, Chichester, 1983, ch. 18, pp. 585–648.
22 K. Fujimori and S. Oae, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1335.
23 Reference 17, Vol. II/9b, p. 324; Vol. II/17b, pp. 510–521.
24 S. F. Nelsen, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1005.
25 P. M. Blum, A. G. Davies and R. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1979, 217.
26 A. G. Davies and R. Sutcliffe, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1483.
27 R. Sutcliffe and K. U. Ingold, *J. Am. Chem. Soc.*, 1981, **103**, 7686.
28 H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575.
29 V. Malatesta, D. Forrest and K. U. Ingold, *J. Phys. Chem.*, 1978, **82**, 2370.
30 R. Sustmann, H. Trill and D. Brandes, *Chem. Ber.*, 1977, **110**, 245, 255.
31 P. G. Webb and J. A. Kampmeier, *J. Am. Chem. Soc.*, 1971, **93**, 3730.
32 M. P. Bertrand, H. Oumar-Mahamet and J. M. Surzur, *Tetrahedron Lett.*, 1985, **26**, 1209; *Bull. Soc. Chim. Fr.*, 1985, 115.
33 R. A. Merrill, Ph.D. Thesis, Yale University, 1986 (*Diss. Abstr. Int., B*, 1987, **47**, 3372).
34 N. Muramoto, T. Ochiai, O. Simamura and M. Yoshida, *Chem. Commun.*, 1968, 717.
35 D. Griller, J. W. Cooper and K. U. Ingold, *J. Am. Chem. Soc.*, 1975, **97**, 4269.
36 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1976, **9**, 13.
37 Reference 17, Vol. II/9b, pp. 303–310; Vol. II/17b, pp. 492–501.
38 L. Bonnazola, S. Fenistein and R. Marx, *Mol. Phys.*, 1971, **22**, 689.
39 G. W. Neilson and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1405.
40 C. Filliatre, M. Baratchart, J. J. Villenave and R. Jaouhari, *Tetrahedron Lett.*, 1982, **23**, 3487.
41 K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 1383.
42 Reference 17, Vol. II/9b, pp. 80–87; Vol. II/17b, pp. 124–126.
43 S. Deycard, L. Hughes, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1987, **109**, 4954.
44 S. Deycard, J. Lusztyk, K. U. Ingold, F. Zerbetto, M. Z. Zgierski and W. Siebrand, *J. Am. Chem. Soc.*, 1988, **110**, 6721.
45 L. J. Johnston and K. U. Ingold, *J. Am. Chem. Soc.*, 1986, **108**, 2343.
46 J. E. Bennett and J. A. Howard, *Chem. Phys. Lett.*, 1971, **9**, 460.
47 H. G. Korth, unpublished data; see also ref. 9.
48 The photo-cleavage of anhydrides to produce acyl and acyloxyl radicals is a well established reaction; see, *e.g.*, J. D. Coyle, *Chem. Rev.*, 1978, **78**, 97; R. S. Givens and N. Levi, in *The Chemistry of Acid Derivatives: Supplement B*, ed. S. Patai, Wiley, Chichester, 1979, Part 1, ch. 11, p. 641.
49 A. G. Neville, unpublished results.
50 A. G. Davies, D. Griller, K. U. Ingold, D. A. Lindsay and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1981, 633; D. Griller, K. U. Ingold and J. C. Walton, *J. Am. Chem. Soc.*, 1979, **101**, 758; R. Sustmann and H. Schmidt, *Chem. Ber.*, 1979, **112**, 1440.
51 Y. Ogata, K. Tomizawa and K. Furuto, in *The Chemistry of Peroxides*, ed. S. Patai, Wiley, Chichester, 1983, ch. 21, pp. 711–775.
52 A. G. Neville, C. E. Brown, D. M. Rayner, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1989, **111**, 9269.
53 N. G. Saha, U. S. Nandi and S. R. Palit, *J. Chem. Soc.*, 1956, 427.
54 See: R. Sustmann and H. G. Korth, in *Methoden der Organischen Chemie* (*Houben-Weyl*), ed. J. Falbe, Thieme, Stuttgart, 1985, Vol. E5, Part 1, pp. 193–466.
55 See: ref. 54, pp, 587–609.
56 G. E. Gream and A. K. Serelis, *Aust. J. Chem.*, 1978, **31**, 863.
57 J. P. Letourneux, B. Gautheron and R. Broussier, *Bull. Soc. Chim. Fr.*, 1975, 2171.
58 F. Bohlmann and M. Brehm, *Chem. Ber.*, 1979, 112, 1071.
59 P. Four and F. Guibe, *J. Org. Chem.*, 1981, **46**, 4439.
60 C. Jutz, *Chem. Ber.*, 1958, **91**, 1867.
61 H. Pielartzik, B. Irmisch-Pielartzik and T. Eicher, in *Methoden der Organischen Chemie* (*Houben-Weyl*), ed. J. Falbe, Thieme, Stuttgart, 1985; Vol. E5, Part 1, pp. 639–640.
62 H. Bornowski, in *Methoden der Organischen Chemie* (*Houben-Weyl*), ed. J. Falbe, Thieme, Stuttgart, 1983, Vol. E3, pp. 290–292.

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