

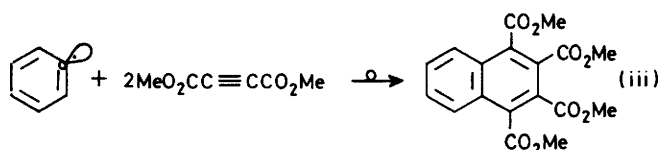
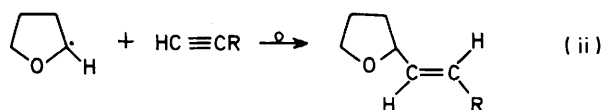
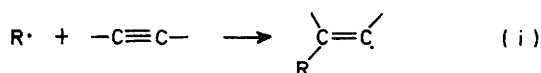
Electron Spin Resonance Studies of Radical Addition to Alkynes and Intramolecular Reactions of Vinyl Radicals

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E.s.r. spectra are described of radicals formed by the reactions of some alkynes both with hydroxyl and also with radicals formed from a variety of ethers in the presence of hydroxyl. Vinyl radicals, though not normally detected, are apparently involved, and evidence is presented for their intermolecular addition and intramolecular abstraction reactions. For example, the vinyl radical produced by addition of $\cdot\text{CHMeOEt}$ to $\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}$ reacts to form the allyl radical $\cdot\text{CHMeC}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$, evidently *via* a 1.5 carbon-to-carbon hydrogen shift and fragmentation. Other instances of ready 1.5-shifts (including an oxygen-to-carbon example) are described.

PREVIOUS studies of the reactions between radicals and alkynes suggest that an initial radical addition to the triple bond [reaction (i)] may be followed by an interesting variety of reactions of the vinyl radicals so formed. Thus, on the basis of product studies, it has been shown that for $\text{R} = \text{tetrahydrofuran-2-yl}^1$ and $\cdot\text{CMe}_2\text{OH}^2$ addition is followed by intermolecular hydrogen abstraction to give substituted alkenes [*e.g.* reaction (ii)]. In contrast, when $\text{R} = \text{aryl}$, the first formed vinyl radical adds to a second molecule of alkyne to give a further vinyl radical which effects an intramolecular homolytic substitution reaction [*cf.* reaction (iii)].³



In a few instances, e.s.r. spectroscopy has been employed in studies of radical intermediates formed in the reactions of alkynes. For example, Neta and Fessenden⁴ have shown that the hydrated electron reacts with butynedioate anion ($^-\text{O}_2\text{CC}\equiv\text{CCO}_2^-$) to give the

¹ E. Montandon and R. Lalande, *Bull. Soc. chim. France*, 1974, 2635.

² G. O. Schenck and R. Steinmetz, *Naturwiss.*, 1960, 43b, 514.

³ B. D. Baigrie, J. Brennan, J. I. G. Cadogan, J. Cook, and J. T. Sharp, *J.C.S. Perkin I*, 1975, 1060.

vinyl radical $^-\text{O}_2\text{CCH}=\text{C}(\text{CO}_2^-)\cdot$ (with the β -hydrogen *trans* to the unpaired electron, as judged by its splitting of 4.9 mT) and that hydroxyl reacts to give $\cdot\text{CH}(\text{CO}_2^-)-\text{CO}-\text{CO}_2^-$, presumably *via* the first formed vinyl radical $\cdot\text{C}(\text{CO}_2^-)=\text{C}(\text{OH})\text{CO}_2^-$. Vinyl radicals have also been detected⁵ when alkynes are bombarded with γ -rays or with hydrogen atoms (the spectra suggest that, in some instances, the vinyl radicals produced have linear, rather than bent, structures). E.s.r. evidence⁶ suggests that reaction of $\cdot\text{OH}$ with $\text{HC}\equiv\text{CCH}_2\text{OH}$ leads to hydrogen atom abstraction [to give $\text{HC}\equiv\text{CCH}(\text{OH})\cdot$] rather than addition, and when the same reaction is carried out in the presence of thiols (RSH), radicals of the type $\cdot\text{CH}(\text{SR})-\text{CH}(\text{SR})\text{CH}_2\text{OH}$ are produced,⁷ evidently *via* addition of first formed $\text{RS}\cdot$.

We have examined the reactions of some alkynes, and particularly propynoic and butynedioic acids, with the hydroxyl radical (from $\text{Ti}^{\text{III}}-\text{H}_2\text{O}_2$ in an aqueous flow system) and with radicals formed by reaction of hydroxyl with other substrates. Attention is focused here on the reactions of some ether-derived radicals.

RESULTS AND DISCUSSION

Reactions of the Hydroxyl Radical.—When propynoic acid was included in the $\text{Ti}^{\text{III}}-\text{H}_2\text{O}_2$ flow system at pH *ca.* 1, two radicals were detected (see Table 1 and Figure 1). Both radicals exhibit e.s.r. parameters expected for allyl-type structures, with splittings of *ca.* 1.2 mT from terminal hydrogen atoms and of *ca.* 0.4 mT

⁴ P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1972, 76, 1957.

⁵ G. W. Neilson and M. C. R. Symons, *J.C.S. Perkin II*, 1973, 1405.

⁶ W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

⁷ T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1971, 93, 908.

from hydrogen on the central carbon (*cf.* allyl,⁸ 1-hydroxyallyl⁹). The magnitude of the *g* factors, and the observation that the terminal hydrogen splittings are slightly lower than those in allyl itself, are consistent with there being CO₂H groups attached to sites bearing significant spin density. These findings can be satisfactorily explained if reaction between ·OH and propynoic acid proceeds as in Scheme 1 to give the two allyl-type radicals (1) and (2). Initial attack by ·OH at each alkynic carbon is followed by attack of the vinyl radicals thus formed on more substrate; 1,5-shifts from oxygen to carbon produce allyl radicals with the appropriate number of hydrogen splittings of 'terminal' and 'central' type. The ratio of the steady-state concentrations of (1) and (2) is 3 : 2, consistent with preferential attack of hydroxyl at the less hindered carbon in the alkyne. No evidence was obtained that the intermediate vinyl radicals can themselves attack the more hindered end of propynoic acid.

Evidence for the mechanism and analysis outlined in Scheme 1 was obtained by carrying out the reactions in deuterium oxide instead of water. The proton-splittings

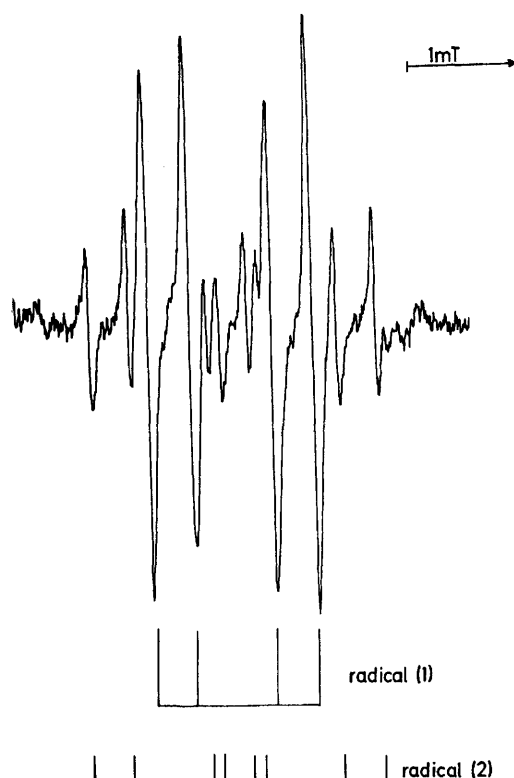


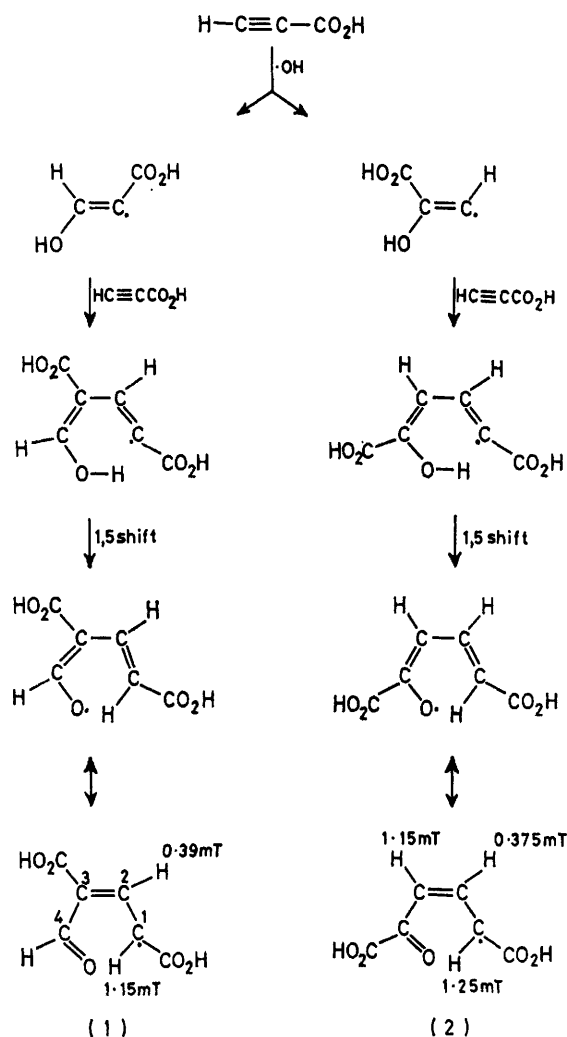
FIGURE 1 E.s.r. spectra of radicals (1) and (2) formed in the reaction between HO· and propynoic acid at pH 1

of 1.15 and 1.25 mT in radicals (1) and (2) were replaced by deuterium splittings of 0.18 and 0.19 mT, respectively. This is consistent with the expected rapid exchange with

⁸ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **1963**, **39**, 2147.

⁹ A. J. Dobbs, B. C. Gilbert, H. A. H. Laue, and R. O. C. Norman, *J.C.S. Perkin II*, **1976**, 1044.

solvent of the hydroxyl protons in the species which undergo 1,5-shifts, so that ²H replaces ¹H at C-1 in radicals (1) and (2).



SCHEME 1

It is interesting to note that, as judged by the magnitudes of the hydrogen splittings, most of the spin density in radicals (1) and (2) is located at positions 1 and 3 (*i.e.* that they are of allyl type) despite the presence of substituents which may provide extended conjugation [*e.g.* -CO-CO₂H in (2)]. This is understandable since carbonyl and carboxy-groups are not particularly effective spin-withdrawing substituents;¹⁰ *i.e.* radicals of the type (1) are best represented as O=C-Ċ-C=C ↔ O=C-C=C-Ċ rather than ·O-C=C-C=C. A further possibility is that conjugation is reduced by twisting around C-3-C-4.

Butynedioic acid reacted with ·OH at pH 1 to give a mixture of radicals in which the spectra from two were dominant (Table 1). One had a doublet splitting (1.41 mT) which was replaced by a deuterium splitting when

¹⁰ (a) H. Fischer, *Z. Naturforsch.*, (a) **1964**, **19a**, 866; (b) **1965**, **20a**, 428.

the reaction was carried out in $^2\text{H}_2\text{O}$. The spectrum increased in intensity when the concentration of substrate was increased, and the spectra from the minor

the 1,5-shift to radical (3), since the vinyl-type spectrum did not diminish in intensity as that from (3) increased. When this reaction was carried out at pH 8, the

TABLE 1
E.s.r. spectra of radicals formed by reaction of alkynes with the hydroxyl radical ^a

Substrate	Hyperfine splittings $a(\text{H})/\text{mT}^b$	g^c	Radical: ^d
$\text{HC}\equiv\text{C}-\text{CO}_2\text{H}$	(i) 1.15 (1), 0.39 (1)	2.003 8	$\cdot\text{CH}(\text{CO}_2\text{H})-\text{CH}=\text{C}(\text{CO}_2\text{H})-\text{CHO}$ (1)
	(ii) 1.25 (1), 1.15 (1), 0.375 (1)	2.003 6	$\cdot\text{CH}(\text{CO}_2\text{H})-\text{CH}=\text{CH}-\text{CO}-\text{CO}_2\text{H}$ (2)
$\text{HO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}^e$	(i) 1.41 (1)	2.002 9	$\cdot\text{CH}(\text{CO}_2\text{H})-\text{C}(\text{CO}_2\text{H})=\text{C}(\text{CO}_2\text{H})-\text{CO}-\text{CO}_2\text{H}$ (3)
$\text{HC}\equiv\text{C}-\text{CH}_2\text{OH}$	(ii) singlet 1.78 (1), 0.99 (1), 0.10(1)	2.003 3 2.003 6	$\text{XC}(\text{CO}_2\text{H})=\text{C}(\text{CO}_2\text{H})\cdot$ $\cdot\text{CH}(\text{OH})-\text{C}\equiv\text{CH}$ (4)
	(i) 1.75 (1), 0.68 (2), 0.095(1)	2.002 9	$\cdot\text{CH}(\text{OH})-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ (5)
$\text{HOCH}_2-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$	(ii) 1.91(1), 2.62(2), 0.30(2)	2.003 9	$\cdot\text{CH}(\text{CH}_2\text{OH})-\text{CO}-\text{CH}_2\text{OH}$ (6)

^a From $\text{Ti}^{\text{III}}-\text{H}_2\text{O}_2$ at pH ca. 1. ^b ± 0.01 mT. ^c ± 0.001 . ^d For comments on detailed assignment and geometrical isomerism, see text. ^e Other weak signals detected; see text

radicals decreased. We infer that this radical has structure (3) (see Table 1) and that it arises by a mechanism similar to that in Scheme 1 in which two molecules

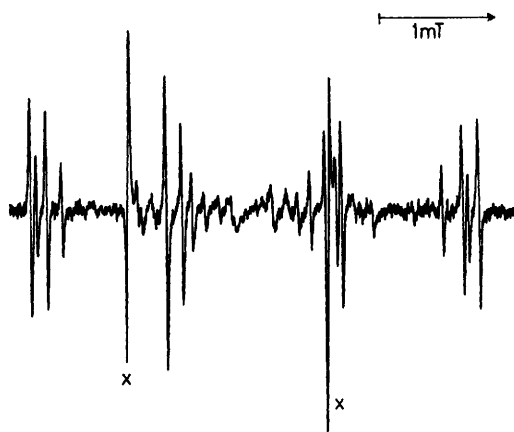


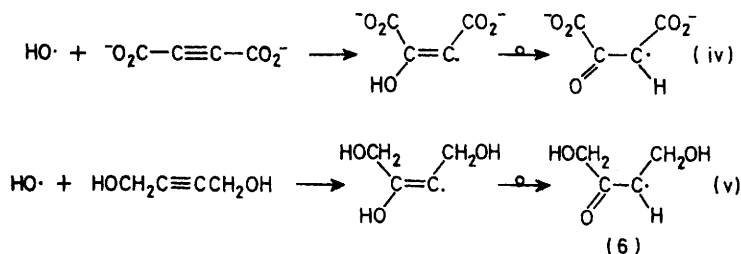
FIGURE 2 E.s.r. spectrum (in emission) of the radical $\cdot\text{CH}(\text{CO}_2^-)\cdot\text{CO}\cdot\text{CO}_2^-$ formed in the reaction between $\text{HO}\cdot$ and butynedioate anion at pH 8 (lines marked x): the absorption spectra are derived from added 1,4-dioxan and are attributed to isomeric forms of (15; $\text{R} = \text{CO}_2^-$)

of substrate are involved. The second radical, which gave only a singlet, seems likely to be of vinyl type, and

spectrum detected had $a(1\text{ H})$ 1.77 mT, g 2.004 5 and was seen in emission [Figure 2 shows this spectrum together with absorption spectra derived from a second substrate (1,4-dioxan) added for reference purposes; the nature of these signals is discussed later.] No corresponding spectrum was observed when the experiment was carried out in D_2O .

The radical formed from $\cdot\text{OH}$ and butynedioate anion is evidently $\cdot\text{CH}(\text{CO}_2^-)-\text{CO}-\text{CO}_2^-$, as detected previously by Neta and Fessenden ⁴ (who also generated this species from $\cdot\text{OH}$ and oxobutanedioic acid). The radical evidently arises *via* reaction (iv). Though the detailed mechanism of the (formal) 1,3-hydrogen shift remains to be clarified we believe that base-catalysed tautomerism may be involved. It seems likely that the isomerisation is favoured over intermolecular reaction, when compared with reaction at pH 1, since attack of a vinyl radical on a further molecule of substrate is retarded by the presence of negative charge on each.

Reaction of $\text{HC}\equiv\text{C}-\text{CH}_2\text{OH}$ with $\cdot\text{OH}$ at pH 1 gave the radical $\text{HC}\equiv\text{C}-\dot{\text{C}}\text{HOH}$ (4), as reported previously;⁶ as judged by $a(\alpha\text{-H})$ and by the alkyne hydrogen splitting, the canonical structure $\cdot\text{CH}=\text{C}=\text{CH}(\text{OH})$ makes a significant contribution to the resonance hybrid. The reaction of butyne-1,4-diol at pH 1 gave two radicals.



possibly therefore either $\text{HOC}(\text{CO}_2\text{H})=\text{C}(\text{CO}_2\text{H})\cdot$ or $\text{HOC}(\text{CO}_2\text{H})=\text{C}(\text{CO}_2\text{H})-\text{C}(\text{CO}_2\text{H})=\text{C}(\text{CO}_2\text{H})\cdot$; if the latter is the explanation, then it is likely that the radical detected is not the geometrical isomer which leads *via*

One was identified as the radical (5) [*cf.* the splittings for (4)], formed by the expected hydrogen-atom abstraction. The other had splitting constants and g factor in the regions expected for an α -carbonyl-conjugated

radical ^{10b,11} and we infer that it is radical (6), formed by reaction (v) which incorporates a 1,3-shift related to that discussed above.

Reaction of Ether-derived Radicals with Alkynes.—When ethers are oxidised with the Ti^{III}-H₂O₂ system,

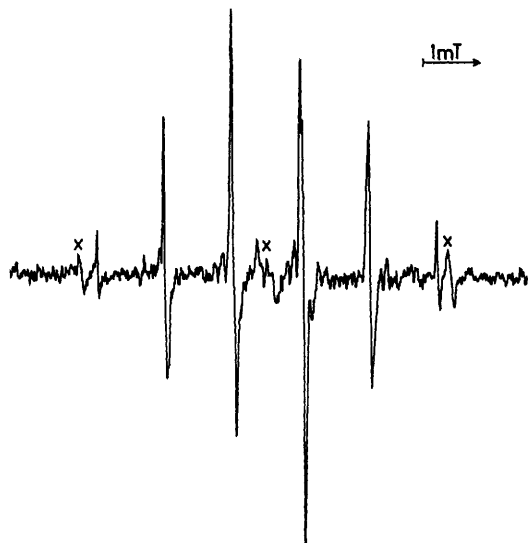
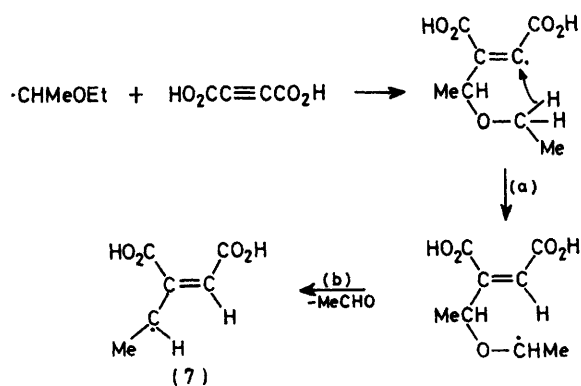
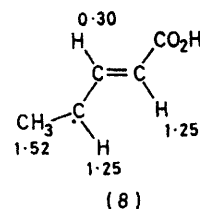


FIGURE 3 E.s.r. spectrum of the radical $\cdot\text{CHMe-C(CO}_2\text{H)=CHCO}_2\text{H}$, formed in the reaction between $\cdot\text{CHMeOEt}$ and butynedioic acid at pH 1 (peaks marked \times are unassigned)

e.s.r. spectra can be detected from radicals formed by abstraction of hydrogen by the electrophilic hydroxyl radical mainly from the carbon atom(s) adjacent to oxygen (see ref. 12 and references therein). We have carried out such reactions in the presence of added alkynes and have found that the spectra of the ether-derived radicals can be completely removed. For most of the ethers employed, the new spectra obtained were straightforward and could be satisfactorily analysed, but in a few cases (*e.g.* with $\cdot\text{CH}_2\text{OMe}$, from dimethyl ether)

(10^{-2}M) at pH 1 proved to a certain extent typical. In this reaction, the ether was kept in considerable excess to ensure that all $\cdot\text{OH}$ radicals were scavenged by the ether (to give mainly $\cdot\text{CHMeOEt}$) rather than by the alkyne (see earlier), and we believe that the e.s.r. spectra detected arise from reaction of the ether-radical with the alkyne. The spectrum detected (see Figure 3) comprises mainly the signal of a radical with $a(1\text{ H})$ 1.33, $a(4\text{ H})$ 1.29 mT, g 2.002 9, together with some weaker, unanalysable lines. The spectrum was unaffected when the oxidation was carried out in D₂O.

On the basis of the arguments presented previously, we conclude that an allyl-type radical (7) is responsible for the spectrum and suggest that it arises as in Scheme 2. Unambiguous assignment of the individual terminal protons in (7) to the splittings of 1.33 and 1.29 mT is impossible, as is assignment to one geometric isomer rather than another. With propynoic acid as substrate, the radical detected had $a(3\text{ H})$ 1.52, $a(2\text{ H})$ 1.25, $a(1\text{ H})$ 0.30 mT, g 2.003 2, and is similarly assigned to the radical (8).



SCHEME 2

the spectra were complex and defied unambiguous analysis.

The behaviour of the Ti^{III}-H₂O₂ system with mixtures of diethyl ether (*ca.* $2 \times 10^{-1}\text{M}$) and butynedioic acid

Scheme 2 involves initial ready attack of the ether-derived radical on the alkyne, a reaction which may be assisted by the presence of $+M$ and $-M$ groups, respectively, in the reagents. This is followed by a 1,5-hydrogen shift (*cf.* the 1,5-shifts discussed above) and loss of acetaldehyde [though steps (a) and (b) may be concerted]. The internal abstraction reaction may well be facilitated by the delocalisation of the unpaired electron in the incipient radical onto an oxygen atom, and the fragmentation is presumably favoured by the stabilities of the allyl radical and aldehyde obtained.

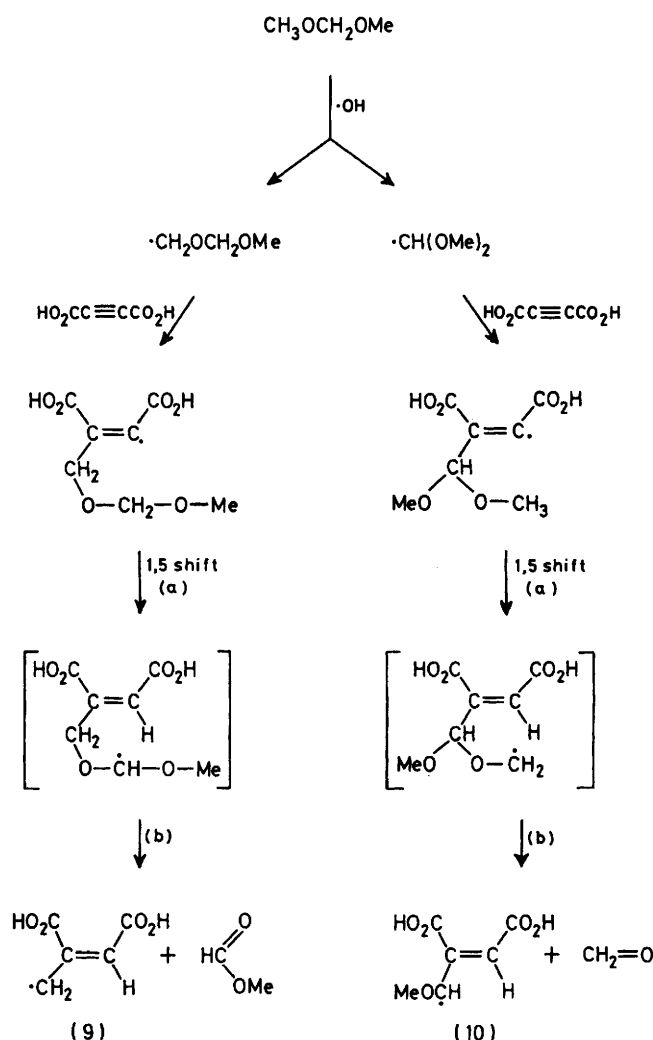
Similar behaviour was observed for other radicals generated, including those from dimethoxymethane [$\cdot\text{CH}_2\text{OCH}_2\text{OMe}$ and $\cdot\text{CH(OMe)}_2$], to give radicals (9) and (10) [*cf.* Scheme 3], and also those from di-isopropyl ether, tetrahydrofuran, trioxan, and paraldehyde (Table 2). The reactions were also carried out with the butynedioate anion at pH *ca.* 8 and, in general, spectra closely similar to those reported in Table 2 were detected.

For the cyclic examples, ring opening of adducts is evidently involved; for example, for tetrahydrofuran we suggest that the reaction sequence is as outlined in Scheme 4. In (11), the three hydrogens with a splitting of 1.24 mT are presumably the (β) CH_2 protons attached to the allyl fragment, together with one of the terminal allyl protons (the other of which has a splitting of 1.31 mT); splittings from the γ - CH_2 protons are also detected.

¹¹ D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 7978.

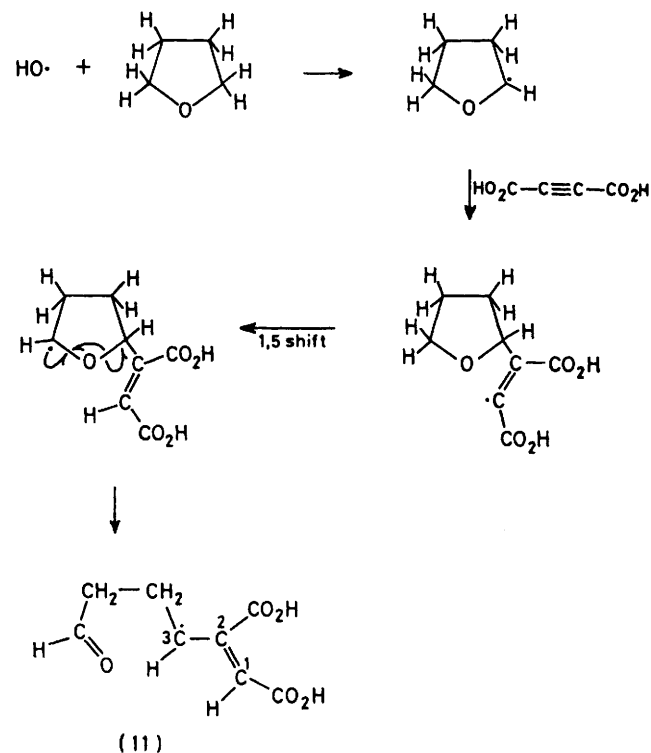
¹² A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. (A)*, 1971, 124.

For this spectrum, as with others, asymmetry in some of the lines and traces of other allyl-type signals pre-



sumably indicate that various geometrical isomers are present (formed by rotation about C-1-C-2 and/or C-2-C-3); unambiguous assignment of the major radical to one specific isomer is not possible.

When $\cdot\text{OH}$ reacts with 1,3-dioxolan under typical flow system conditions both the 1,3-dioxolan-4-yl and -2-yl



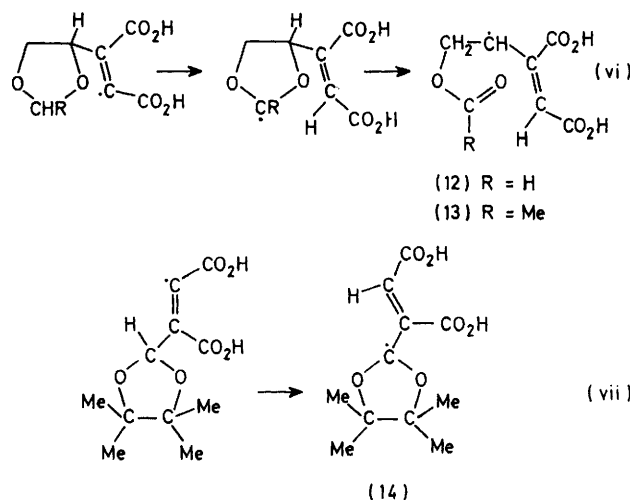
radicals are detected, the former being present in somewhat higher concentration. In the presence of butynedioic acid a mixture of signals is obtained in which the spectrum attributed to an allyl-type radical [assigned

TABLE 2
E.s.r. spectra of radicals obtained by the reaction of ether-derived radicals ^a with butynedioic acid

Reactant radical	Hyperfine splittings <i>a</i> /mT ^b	<i>g</i> ^c	Radical ^d
$\cdot\text{CHMeOEt}$	1.33 (1), 1.29 (4)	2.002 9	$\cdot\text{CHMe}-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$ (7)
$\cdot\text{CH}_2\text{OCH}_2\text{OMe}$	1.25 (2), 1.47 (1)	2.003 1	$\cdot\text{CH}_2-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$ (9)
$\cdot\text{CH}(\text{OMe})_2$	1.01 (1), 1.29 (1)	2.003 3	$\cdot\text{CH}(\text{OMe})-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$ (10)
$\cdot\text{CMe}_2\text{OCHMe}_2$	1.40 (3), 1.25 (1), 1.13 (3)	2.003 1	$\cdot\text{CMe}_2-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$
Tetrahydrofuran-2-yl	1.31 (1), 1.24 (3), 0.075 (2)	2.003 0	$\text{HC}(\text{O})\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$ (11)
1,3-Dioxolan-4-yl	1.37 (2), 1.20 (2), 0.075 (1)		$\text{HC}(\text{O})\text{OCH}_2\dot{\text{C}}\text{H}-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$ (12)
2-Methyl-1,3-dioxolan-4-yl	1.37 (2), 1.20 (2)		$\text{MeC}(\text{O})\text{OCH}_2\dot{\text{C}}\text{H}-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$ (13)
4,4,5,5-Tetramethyl-1,3-dioxolan-2-yl	1.30	2.002 9	(14)
	(i) 2.75 (1), 1.22 (1), 0.18 (1)	2.003 0	(15)
1,4-Dioxanyl	(ii) 2.50 (1), 1.16 (1), 0.26 (1)	2.003 3	
1,3,5-Trioxanyl	1.33 (1), 1.13 (1), 0.05 (2)	2.003 3	$\text{HC}(\text{O})\text{OCH}_2\text{O}\dot{\text{C}}\text{H}-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$
2,4,6-Trimethyl-1,3,5-trioxanyl	1.27 (4), 0.025 (1)	2.003 2	$\text{MeC}(\text{O})\text{OCHMeO}\dot{\text{C}}\text{H}-\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$

^a Generated from ethers with $\text{Ti}^{\text{III}}-\text{H}_2\text{O}_2$ at pH *ca.* 1. ^b ± 0.01 mT. ^c ± 0.000 1. ^d For comments on detailed assignment and geometrical isomerism, see text.

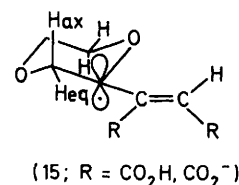
structure (12)] can be clearly recognised. We believe that this is formed from 1,3-dioxolan-4-yl *via* a sequence involving addition and 1,5 hydrogen shift as described for other ethers [reaction (vi); R = H]. The fate of the 1,3-dioxolan-2-yl radical could not be established. With 2-methyl-1,3-dioxolan the complex spectrum detected included a signal closely similar to that from (12) but lacking the long range formyl proton splitting: we assign it to the corresponding radical (13) formed *via* addition of 2-methyl-1,3-dioxolan-4-yl and subsequent abstraction and fragmentation [reaction (vi); R = Me].



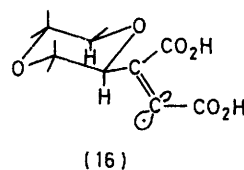
For the adduct from the 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl radical, different behaviour is observed. The radical detected has a single allyl-type proton splitting and is tentatively assigned the structure (14). In this case a 1,5-shift cannot occur, and a formal 1,3-shift [reaction (vii)] appears to have taken place. Concerted reactions of this type are not well documented and, in contrast to the 1,5-shifts noted above, are unexpected; although the shift may proceed in concerted fashion, presumably assisted by the developing conjugation in (14), another possibility is that the radical adduct undergoes an *intermolecular* hydrogen-atom abstraction (*e.g.* with more of the dioxolan) to give an alkene which reacts (*e.g.* with $\cdot\text{OH}$) to give (14).

Rather more surprising, perhaps, is that a similar process appears to occur for the 1,4-dioxanyl radical adduct, although a 1,5-shift would have been expected (*cf.* reaction of tetrahydrofuran-2-yl). Thus, the two radicals detected by e.s.r. each have one allyl-type splitting and two other splittings [2.75, 0.18 mT in one case, 2.50, 0.26 mT in the other (data for pH 1, *cf.* Table 2; Figure 2 shows the essentially identical spectra at pH *ca.* 8)]; we tentatively assign these to geometric isomers of the allylic species (15; R = CO₂H). We believe that the large splitting in each case arises from the (β) axial proton, which makes a small dihedral angle with the orbital of the unpaired electron and which hence has a significant hyperconjugative interaction (which should depend approximately on $\cos^2\theta$). Much

smaller splittings would be expected from the equatorial protons (dihedral angle *ca.* 90°) and the γ -protons in the ring. In 1,4-dioxanyl itself,¹³ the β -proton splittings



are *ca.* 4.2 and 0.4 mT, respectively (individual splittings are not resolved and interconversion occurs, at room temperature, at an intermediate rate which leads to a 1 : broad : 1 pattern) and the γ -proton splitting is 0.13 mT (2 H). For a radical with less rapid flexible motion and only *ca.* 50% of the unpaired electron density located at the relevant position in the ring [*i.e.* for (15)] the assignment $a(\beta\text{-H}_{\text{ax}})$ 2.75 (2.5) mT, and $a(\beta\text{-H}_{\text{eq}})$ or $a(\gamma\text{-H}_{\text{ax}})$ 0.18 (0.26) mT appears reasonable. Although the radical responsible for the spectrum may indeed be (15), it must be borne in mind that a formal 1,3-shift would then be implied. If this is so then it seems somewhat surprising that the adduct from the 1,4-dioxanyl radical behaves differently from related adducts from cyclic radicals in which 1,5-shifts occur. One possible explanation is that in the adduct between 1,4-dioxanyl and butynedioic acid the vinyl group occupies solely the equatorial position [*cf.* (16)] and not the alternative axial site. Then, as models show, the radical site cannot approach and abstract a hydrogen atom five bonds removed from it. However, for adducts in which the substituent is in an axial site (this may be more easily achieved for other substrates and should certainly be so for five-membered rings) the transition state for 1,5 hydrogen abstraction is readily achieved.



We have also studied the reactions of alkynes with a variety of other radicals, including those of alkyl, hydroxyalkyl, and aryl type. Radicals detected, including first formed vinyl species and those formed by subsequent reactions, will be described in a later publication

EXPERIMENTAL

Experiments were carried out at Bedford College, University of London, and at the University of York. Although the experimental arrangements (notably the design and operation of flow systems) differed somewhat, closely similar results were obtained by both groups of workers.

The e.s.r. spectra were measured on Varian E-3 (York) and E-4 (Bedford College) spectrometers with X-band

¹³ W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4850.

klystrons and 100 kHz modulation. Splitting constants were determined to within ± 0.01 mT, and g -factors to within ± 0.0001 , by comparison with Fremy's salt [$a(N)$ 1.3091 mT,¹⁴ g 2.0055¹⁵]. Both modified and standard Varian mixing chambers were employed, each allowing the simultaneous mixing of three (or two) reactant solutions *ca.* 0.04 s before passage into the spectrometer cavity. One stream contained titanium(III) chloride (0.006M), the second hydrogen peroxide (0.03M), and the third the alkyne (*ca.* 0.15M) or a mixture of the alkyne (0.15M) and an ether (0.6M). For most of the experiments, solutions were acidified to pH *ca.* 1 with concentrated sulphuric acid; for reactions at pH *ca.* 8, the sodium salt of ethylenediaminetetra-acetic acid (6 g l⁻¹) was added to the titanium(III) stream and the pH adjusted to the required value

by addition of potassium carbonate. At York, experiments with D₂O (Ryvan Chemicals Ltd.; 99.8%) were performed on a small scale two-stream flow system employing motor-driven 200 ml syringes [containing Ti^{III} and H₂O₂ solutions, respectively (as above) with substrate in both streams] and an all-glass mixing chamber and cell. At Bedford College the D₂O experiments were conducted in the same manner as those with H₂O but with the Varian two-port mixing chamber, the flow system being driven by a peristaltic pump with the substrates in both streams. All solutions were deoxygenated with a nitrogen purge prior to mixing. All compounds were commercial materials and were used without further purification.

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¹⁴ R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

¹⁵ J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.