Radical Addition to Alkynes: Electron Spin Resonance Studies of the Formation and Reactions of Vinyl Radicals

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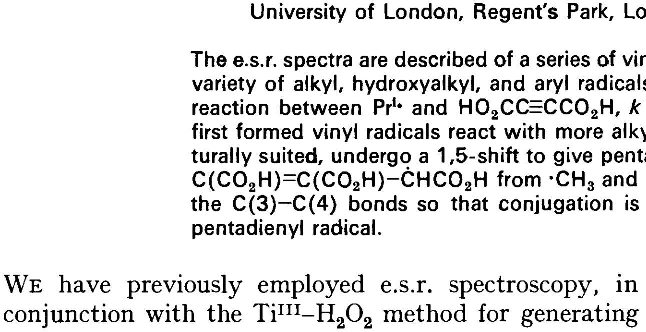
The e.s.r. spectra are described of a series of vinyl radicals XRC=CR• (R = CO_2H, CO_2^-) formed by the addition of a variety of alkyl, hydroxyalkyl, and aryl radicals (X) to butynedioic acid and the corresponding dianion. For the reaction between Pr^{i}• and $HO_2CC{\equiv}CCO_2H$, *k* is estimated as *ca.* 2×10^6 dm^3 mol^{-1} s^{-1}. In acid solution the first formed vinyl radicals react with more alkyne to give further vinyl radicals XRC=CR–CR=CR• which, if structurally suited, undergo a 1,5-shift to give pentadienyl radicals. The spectra of the latter [*e.g.* for $CH_2{=}C(CO_2H){-}C(CO_2H){=}C(CO_2H){-}\dot{C}HCO_2H$ from $\cdot CH_3$ and butynedioic acid] indicate there to be considerable twisting around the C(3)–C(4) bonds so that conjugation is reduced compared to that in the fully conjugated unsubstituted pentadienyl radical.

WE have previously employed e.s.r. spectroscopy, in conjunction with the Ti^{III}–H_2O_2 method for generating radicals in aqueous solution, to characterise intermediates in the reactions of butynedioic and propynoic acids with the hydroxyl radical and with ether-derived radicals.[1] Vinyl radicals such as (1) would be expected to be formed initially, but none were detected. However, the results were consistent with their formation and subsequent rapid reaction; for example, the formation of radical (3) was interpreted as in Scheme 1, in which the vinyl radical (1) undergoes intramolecular 1,5-hydrogen transfer followed by, or concerted with, fragmentation of radical (2) to give a relatively stable allylic species.[1]



SCHEME 1

We have now studied the addition to C≡C of a wider variety of radicals (alkyl, α-hydroxyalkyl, and aryl, as well as further examples of α-alkoxyalkyl) with the aims of characterising intermediate vinyl radicals and exploring the scope of their intramolecular 1,*n*-hydrogen shifts.

RESULTS AND DISCUSSION

As before,[1] we have employed a two-stream aqueous flow system driven by a peristaltic pump. We have generated alcohol- and ether-derived radicals by inclusion of the appropriate parent compound in the Ti^{III}–H_2O_2 system, alkyl radicals by the Ti^{III}–H_2O_2–R_2SO [2] method, and aryl radicals by the Ti^{III}–H_2O_2–HCO_2H–ArN_2^+ method (acid solution) and Ti^{III}(EDTA)–ArN_2^+ method (basic solution).[3] Experiments have usually been carried out in both acid solution (pH 1—2) and in basic solution with EDTA (pH 7.5—9), and with each of two concentrations (*ca.* 0.004 and 0.02M) of the alkyne. The results described here were obtained with butynedioic acid; the use of propynoic acid generally led to weak spectra for which unambiguous analysis was impossible, and no signals were obtained from ethyne itself.

Low Concentrations of Butynedioic Acid.—The inclusion of this alkyne at low concentration in the appropriate redox system usually resulted in the disappearance or diminution of the e.s.r. signal from the radical characteristic of that system (except in the case of aryl radicals, signals from which were not observed [3]) and the appearance of one with *g* close to 2.003 0 (Table 1). We infer that these are the spectra of vinyl radicals (4; R = CO_2H or CO_2^-) and note for the moment that none is structurally suited for the 1,5-hydrogen shift that is characteristic of undetected vinyl radicals. Attempts to add propyl radicals (from Pr_2SO and •OH) and butyl radicals (from the corresponding sulphoxide) to butynedioic acid led to the detection of weak spectra which were not analysable, and there was no evidence for the addition of the allyl radical to the alkyne; when this radical was generated from diallyl sulphoxide its spectrum [*a*(2H) 1.49, *a*(2H) 1.275, *a*(1H) 0.42 mT] was unaffected by the inclusion of the alkyne. No vinyl radical could be detected from the addition of the 2-methylphenyl radical (generated from the 2-methylbenzenediazonium ion); the spectra detected from this substrate are described subsequently.

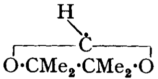
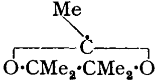
$$X\cdot + RC{\equiv}CR \longrightarrow \underset{(4)}{XCR{=}\dot{C}R} \qquad (1)$$

The resolution of the spectra of the vinyl radicals varied somewhat with pH in the ranges 1—2 and 7.5—9 for (4; R = CO_2H and CO_2^- respectively), and the results in Table 1 refer to optimum conditions. The radicals (4) generally exhibit long-range couplings to both γ-protons (*e.g.*, to the methyl protons when X = Me and to the methylene protons when X = CH_2Me, CH_2OH, CH_2OCMe_3) and δ-protons (*e.g.*, to the methyl protons when X = Me_2CH, Me_3C). A further notable feature is the apparent equivalence of the *ortho-* and *meta*-protons when X = C_6H_5. Comparison with the spectra when X = 2-fluorophenyl suggests that the relatively large splitting in the latter case results from interaction with the ^{19}F nucleus.

There are some significant differences in the long-range proton splittings for the ionised, compared with the protonated, radicals. For example, no γ-proton splitting could be resolved for the radical (4; X = CHMeOH, R = CO_2H) and (from the linewidth) it must be <0.01 mT, whereas the ionised counterpart showed two doublet splittings (0.03 and 0.015 mT), evidently from the γ- and the hydroxy-protons (although individual assignments cannot be made). [The radical (4; X = CH_2OH, R = CO_2^-) also exhibits coupling with the hydroxy-proton.] In contrast, a γ-proton splitting is detectable in (4; X = $CHMe_2$, R = CO_2H) but not in the ionised form. These unusual features could reflect a variety of factors, including the effect of ionisation on the geometry at the radical centre (see later), and the preferred conformation of the group X.

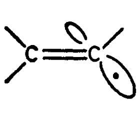
TABLE 1

E.s.r. parameters for vinyl radicals $XCR{=}\dot{C}R$

	R = CO_2H		R = CO_2^-	
X	Hyperfine splitting (mT) [a]	g [b]	Hyperfine splitting (mT) [a]	g [b]
Me	0.10 (3 H)	2.0028	0.07 (3 H)	2.0028
$MeCH_2$	0.105 (2 H), 0.03 (3 H)	2.0029	0.04 (3 H), 0.06 (2 H)	2.0029
Me_2CH	0.04 (1 H), 0.038 (6 H)	2.0027	0.04 (6 H)	2.0029
Me_3C	0.06 (9 H)	2.0027	0.055 (9 H)	2.0029
CH_2OH	0.065 (2 H)	2.0029	0.025 (3 H)	2.0029
CHMeOH	0.04 (3 H)	2.0029	0.045 (3 H), 0.03 (1 H), 0.015 (1 H)	2.0029
CMe_2OH	0.06 (6 H)	2.0029	0.03 (6 H)	2.0029
C_6H_5	0.02 (4 H)	2.0027	0.02 (4 H)	2.0028
2-FC_6H_4	0.31 ($1^{19}F$)	2.0029	0.28 ($1^{19}F$), 0.03 (3 H)	2.0028
Me_3COCH_2	0.075 (2 H)	2.0029	0.045 (2 H)	2.0029
	0.135 (1 H)	2.0030	0.10 (1 H)	2.0029
	0.055 (3 H)	2.0030	0.045 (3 H)	2.0031

[a] ±0.01 mT. [b] ±0.0001.

The e.s.r. parameters for the radicals (4) do not allow us to choose between structures in which the unpaired electron occupies an sp^2-orbital (5) and an essentially *p*-type orbital (6). The vinyl radical itself is known to possess the former structure, with non-equivalent β-proton splittings of 3.4 and 6.8 mT in the solid state at 4 K [4] (though rapid exchange renders these apparently equivalent in the liquid phase at −180 °C [5]). The vinyl radicals $\cdot C(CMe_3){=}CHSiMe_3$ and $\cdot C(SiMe_3){=}CHSiMe_3$ are attributed [6] σ-structures (5) on account of the magnitude of the β-hydrogen splitting (*ca.* 7.0 mT, assigned to the *trans*-β-H), whereas the more hindered radical $\cdot C(SiMe_3){=}C(SiMe_3)_2$ is assigned the *p*-type structure (6) on account of the two equivalent β-Si splittings and the low α-^{13}C splitting. INDO Calculations for a variety of vinyl radicals predict [7] that only if the α-substituent is less electronegative than carbon (*e.g.* BH_2) is a linear geometry (6) to be expected. However, a *p*-type structure has been proposed [8] for $H_2C{=}C(CO_2H)\cdot$ in which the two β-protons interact equally [a(2H) 5.3 mT] [*cf.* also $^-O_2CCH{=}C(CO_2^-)\cdot$, from e^- and butynedioic acid, which has a(β-H) 4.979 mT, but for which a σ-type structure was suggested [9]]. The α-carboxy-function in (4) apparently causes an increase in the g value [*cf.* also 2.002 83 for $^-O_2CCH{=}C(CO_2^-)\cdot$] in [9] comparison with g *ca.* 2.002 2 for both σ and π vinyl radicals lacking this substituent, but the change does not appear to be diagnostic of either a σ- or π-structure.



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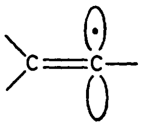
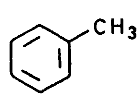


(6)

It is not clear whether the radicals we have detected possess the σ-structure (5), in which case the CO_2H (or CO_2^-) groups could be *cis* or *trans* with respect to each other (or even interconverting rapidly, to give an average set of splittings), or the *p*-type structure (6). It seems unlikely that a fixed geometry (5) with carboxy-groups *trans* is adopted since intramolecular reaction involving the radical centre and the addend in radicals of this type (see Scheme 1) would be impossible. Instead it appears that either rapid *cis–trans* isomerism takes place [involving (5)] or that the *p*-structure (6) is preferred [*cf.* $CH_2{=}C(CO_2H)\cdot$]; on the basis of evidence available at present, the latter appears to be more likely. In either case, long-range splittings are not unexpected, since the orbital of the unpaired electron is eclipsed by the C(β)–C(γ) bond, a situation which is especially favourable for the onward transmission of spin density.[10]

Further evidence for the ready occurrence of 1,5-hydrogen shifts in appropriately substituted vinyl radicals is derived from the detection of spectra attributed to a substituted benzyl radical in the reactions of 2-methylphenyl (7) with butynedioic acid at low and high pH. At low pH the spectrum detected has a(2H) 1.57, a(1H) 0.61, a(1H) 0.51, a(2H) 0.18, and a(1H) 0.095 mT, with g 2.002 6; this is attributed to the radical (9; R = CO_2H), formed from the undetected vinyl radical (8), with splittings from the methylene protons, *p*-H, *o*-H, *m*-H, and the alkene proton, respectively (*cf.* the parameters from benzyl itself under similar conditions [11]). [At high pH, the spectrum detected is closely similar, with hyperfine splittings 1.59 (2H), 0.61 (1H), 0.51 (1H), 0.18 (2H), and 0.08 (1H) mT, with g 2.002 75, and is attributed to (9; R = CO_2^-), formed similarly.] The close similarity between the splittings for (9; R = CO_2H, CO_2^-) and the appropriate values for benzyl itself [which has, *e.g.*, $a(CH_2)$ 1.59, $a(p\text{-H})$ 0.61 mT] indicates that the alkene substituent here has little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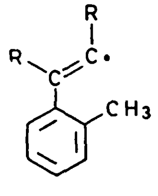
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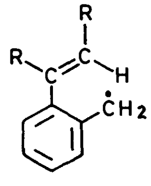
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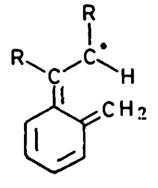
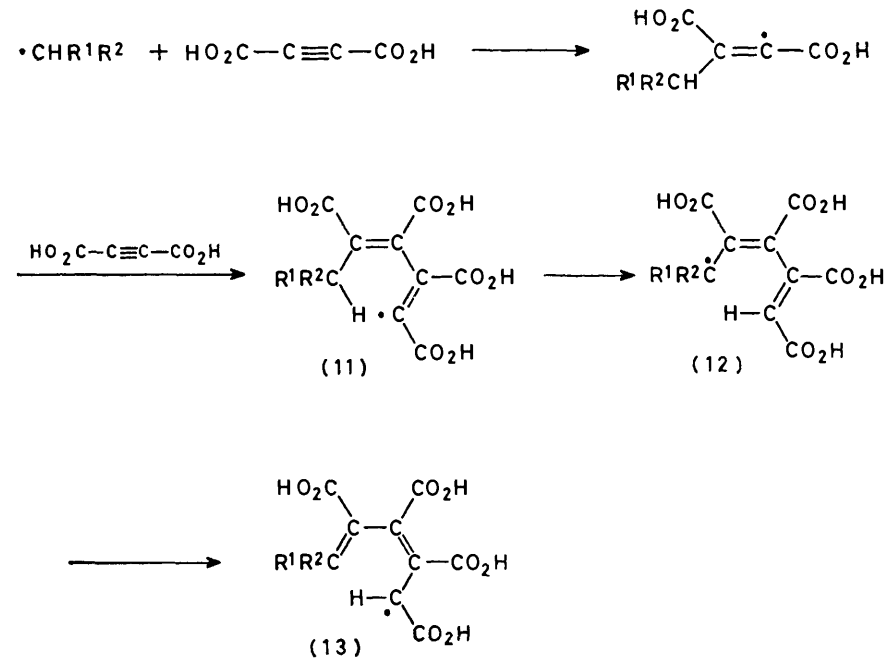

(10)

delocalising ability (*cf.* also the small value of the alkene hydrogen splitting), so that structure (10) does not make a significant contribution to the resonance hybrid. It seems likely that, instead, steric constraints cause there to be considerable twisting around the C(aryl)–C(alkene) bond.


SCHEME 2

Higher Concentrations of Butynedioic Acid.—When experiments involving Me•, $\cdot CH_2OH$, and some related radicals were carried out in the presence of increasing concentrations of butynedioic acid at pH 1—2, the spectrum assigned to the corresponding vinyl radical diminished in intensity and the spectrum of a new radical (two, in the case of reaction with $\cdot CH_2OH$) appeared. The latter was characterised by a relatively large doublet splitting of *ca.* 1.1 mT, as well as smaller splittings. When the alkyne concentration reached *ca.* 0.02M, this was generally the only detectable signal. The spectra are attributed to radicals of the type (13), for reasons discussed in the sequel, and their parameters are in Table 2.

TABLE 2

E.s.r. parameters of radicals assigned the structure $R^1R^2C{=}C(CO_2H){-}C(CO_2H){=}C(CO_2H){-}\dot{C}HCO_2H$, from radicals $\cdot CHR^1R^2$ and butynedioic acid

R^1	R^2	Hyperfine splittings (mT) [a]	g [b]
H	H	1.16 (1 H), 0.24 (1 H), 0.145 (1 H)	2.0032
H	OH	1.085 (1 H), 0.175 (1 H) 1.145 (1 H), 0.08 (1 H)	2.0032 2.0032
H	Me	1.21 (1 H), 0.05 (3 H), 0.02 (1 H)	2.0031
Me	OH	1.15 (1 H), 0.03 (4 H) [c]	2.0033
Me	Me	1.175 (1 H), 0.11 (3 H), 0.06 (3 H)	2.0032
H	$OCMe_3$	1.27 (1 H)	2.0032

[a] ±0.01 mT. [b] ±0.0001. [c] $a(Me) = a(OH)$.

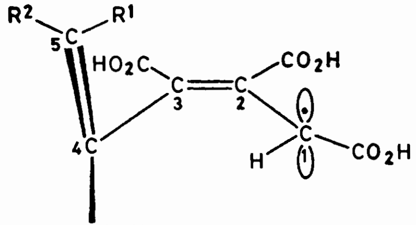
First, the *g*-factors are consistent with radicals of π-type with conjugation to carboxy.[12] Secondly, the large doublet splitting is in the range of the values characteristic of terminal protons in allyl radicals (see earlier). Thirdly, when experiments with the radicals $\cdot CH_3$ and $\cdot CH_2OH$ were carried out in deuterium oxide, none of the proton splittings was affected, indicating that none is associated with a hydroxy- or carboxy-group; this is consistent with the proposed structures (13) and also with their suggested mode of formation in

Scheme 2, in which there is no opportunity for proton exchange with the solvent of those hydrogen atoms which are attached to the terminal carbon atoms of the (formal) pentadienyl chain and which we infer to be those that interact. [When reaction with the radical $\cdot CHMeOH$ was carried out in deuterium oxide, the small quintet splitting was replaced by a quartet; evidently in this case a hydroxy-proton (presumably that in the alcoholic group) interacts to the same extent as the methyl protons.] Finally, radicals of this type were only formed when the initial radical possessed at least one hydrogen atom at the tervalent carbon atom. In contrast, the species formed from $\cdot CMe_2OH$ when the initial vinyl radical disappeared at high alkyne concentrations does not show a large doublet splitting but has a(3H) 0.81, a(3H) 0.68 mT, g 2.003 2; this spectrum has not been assigned. It should also be noted that the spectrum from $Bu^tC(CO_2H)=C(CO_2H)\cdot$ was not removed at high alkyne concentrations, evidently on account of steric retardation of addition by the bulky t-butyl group. The signal from $PhC(CO_2H)=C(CO_2H)\cdot$ also remained effectively unchanged as the concentration of alkyne was increased; this may reflect a similar retardation to further reaction, although it is possible that a small amount of ' dimer ' $PhC(CO_2H)=C(CO_2H)-C(CO_2H)=C(CO_2H)\cdot$ is formed but that this has an identical g value to the ' monomer ' vinyl.

We have deliberately written radical (13) as formed from (12), although at first sight the two would appear to be canonical forms of the same species. This is because the hyperfine splittings show that, as with the benzyl radical (9) discussed earlier, there is not full delocalisation of the unpaired spin as could occur in a fully coplanar pentadienyl radical. We infer instead that radicals (13) [and, by analogy, (12)] cannot achieve the necessary coplanarity for full delocalisation because of steric compressions in the coplanar form; that is, they preferentially adopt a structure (14) in which twisting has occurred about C(3)–C(4), so that the π-orbital associated with the unpaired spin is essentially confined to C(1)—C(3) and the species are allylic radicals. The large doublet-splitting is then assigned to the proton at C(1), and the smaller splittings arise by long-range interactions of the spin [on C(1)—C(3)] with the substituents on C(5) [*cf.* also (9)]. That there are two small doublet splittings in the radical (13; $R^1 = R^2 = H$) then follows because the protons at C(5) are non-equivalently placed with respect to the spin, the two methyl splittings in (13; $R^1 = R^2 = Me$) arise in like manner, and the two species derived from the initial radical $\cdot CH_2OH$ are isomeric structures of the type (13), namely (14; $R^1 = H$, $R^2 = OH$ or $R^1 = OH$, $R^2 = H$).

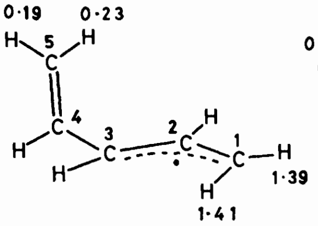
We have carried out INDO calculations [13] on pentadienyl radicals of different geometries and have obtained results in agreement with our interpretation above. In order to simplify the calculations we used pentadienyl itself, $\cdot CH_2-CH=CH-CH=CH_2$, as a model and chose initially *cis*- and *trans*-radicals in which all atoms were held in a plane and then varied the angle of twist around C(3)—C(4). For the planar models, the C–C bond lengths were taken as 0.140 nm; for substantial angles of twist the C(3)–C(4) bond was lengthened to 0.146 nm and the C(4)–C(5) bond was shortened to 0.134 nm. In all calculations the C–H bond length was taken as 0.108 nm.

The calculations reproduce the trends to be expected on twisting [and hence decreasing the extent of conjugation between the C(1)–C(2)–C(3) and the C(4)–C(5) fragments]. For planar geometries, both sets of CH_2 protons [at C(1) and C(5)] give significant calculated splittings (*ca.* 1.1 mT), indicative of a delocalised species with equal spin densities in the p-orbitals on these carbons. As the twisting is introduced however, the splittings from the protons on C(1) increase, and those from the C(5) protons decrease. When θ approaches 90° it is notable that the C(5) protons are predicted to have very small but nevertheless significant couplings close to those observed [*cf.* the structures (15) and (16), with $\theta = 90°$ in each case; the long range ε-couplings should be compared with the values observed for $H_2C=C(CO_2H)-C(CO_2H)=C(CO_2H)-\dot{C}H(CO_2H)$ of 0.24 and 0.145 mT].



(14)

The occurrence of significant spin density at the protons on C(5) is evidently a consequence of overlap between the singly-occupied p-orbital on C(3) and the C(4)–C(5) σ-bond which eclipses it (*cf.*, *e.g.*, ref. 10). Although the assignment of individual splittings in (13; $R^1 = R^2 = H$) must remain tentative, it is interesting to note that the assignment suggested by INDO [*cf.* (15) and (16)] is in agreement with a simple interpretation in which homohyperconjugation [*cf.* structure (17)] is responsible, at least in part, for the long-range interaction.



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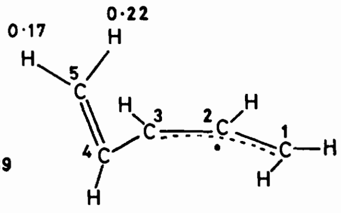
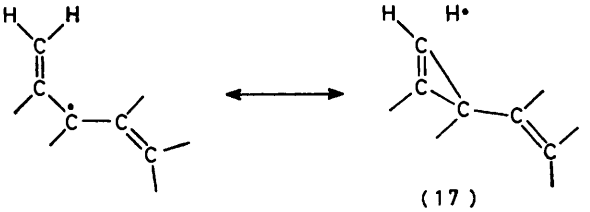


(16)

Models suggest that the pentadienyl radical itself should preferentially adopt a coplanar *trans*-conformation (18), in which there is little strain. If so, its e.s.r. spectrum should exhibit equal splittings for equivalently located pairs of C(1) and C(5) protons. This proved to be so. We generated the radical by irradiating di-t-butyl peroxide in cyclopropane containing penta-1,4-diene at 223 K and obtained a spectrum in which the predominant radical had a(1H) 1.150, a(2H) 1.040, a(2H) 0.968, and a(2H) 0.338 mT, and g 2.002 7 (other weaker resonances were not assigned).* We assign the splittings, respectively, to the proton at C(3), to the pairs of *exo*- and *endo*-protons at C(1) and C(5) (the small difference between them resembles that for the allyl radical, although individual assignment cannot be made), and to the equivalently located protons at C(2) and C(4). It seems likely that the radical has the *trans*-geometry indicated and it is possible that weaker lines detected originate from a smaller amount of *cis*-conformer present, though this was not confirmed.



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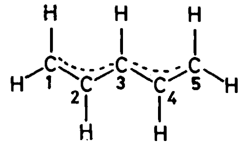

(18)

When the concentration of butynedioic acid was increased in experiments at pH 8, the spectra of the vinyl radicals (4; R = CO_2^-) were essentially unchanged and no new signals could be detected. Evidently addition of the vinyl radical to another molecule of the alkyne is relatively slow owing to the electrostatic repulsion between the doubly negatively charged species.

It is apparent from our previous [1] and present results that the intramolecular 1,5-hydrogen shift involving a vinyl radical is an especially favoured reaction with respect both to the competing intermolecular processes and to alternative 1,n-shifts. Thus, if the initial vinyl radical is structurally suited to a 1,5-shift, this occurs too rapidly to allow the vinyl radical to reach detectable concentration; however, if it is structurally unsuited to such a shift, the vinyl radical may be detected, but if conditions are suitable for the occurrence of addition to more alkyne to give a new vinyl radical (11) which can undergo a 1,5-shift, this occurs sufficiently rapidly that the new vinyl radical is not detectable.

The detection of radicals (4; R = CO_2H and CO_2^-, X = CH_3, CH_2OH, *etc.*) rules out the occurrence to any significant extent of 1,3-hydrogen shifts in these species (even though stabilised allyl and oxygen-substituted allyl radicals would result). The detection of a vinyl radical from the addition of 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl to butynedioic acid (see Table 1) indicates that this species does not undergo a 1,3-shift (as had been tentatively suggested [1] as an explanation for the formation of an allyl-type radical in this system: it seems likely that the reaction involves, instead, addition of two molecules of alkyne followed by a 1,5-shift as observed for other substrates). The case of the adduct from the 1,4-dioxanyl radical, where a 1,3-shift has also been invoked, apparently remains an exception. There is no evidence to suggest that 1,4-shifts occur in vinyl radicals (4; R = CO_2H and CO_2^-, X = Et, Pr^i, Bu^t) although in these cases the (alkyl) radical produced would not be stabilised.

The Rate of Addition of Pr^i *to Butynedioic Acid.*—In a series of experiments with $Pr^i\cdot$ and $HO_2CC{\equiv}CCO_2H$ at pH 1 (employing $[Ti^{III}]_0$ 0.003M, $[H_2O_2]_0$ 0.033M, $[Pr^i{}_2SO]$ 0.055M,† and a three-way flow system with mixing time *ca.* 50 ms) we have studied the dependence of the concentrations of $Pr^i\cdot$ and $Pr^iC(CO_2H){=}C(CO_2H)\cdot$ on the alkyne concentration {up to $[HO_2CC{\equiv}CCO_2H]$ 0.005 5M, when signals from the 'dimer' radical $\cdot CH(CO_2H){-}C(CO_2H){=}C(CO_2H){-}C(CO_2H){=}CMe_2$ become significant}. For the region $[HO_2CC{\equiv}CCO_2H]$ 2 × 10^{-4}—2 % 10^{-3}M, $[Pr^i\cdot]$ decreased to match the approximately linear increase in $[Pr^iC(CO_2H){=}C(CO_2H)\cdot]$, and some typical values are as follows: for [alkyne] = 0.001 1M, $[Pr^i\cdot] = 2.07 \times 10^{-6}$ and [vinyl] = 0.59×10^{-6}M, for [alkyne] = 0.002 2M, $[Pr^i\cdot] = 1.66 \times 10^{-6}$ and [vinyl] = 1.23×10^{-6}M. When $[HO_2CC{\equiv}CCO_2H]$ reached 0.004 4M, the concentration of the vinyl radical levelled off at *ca.* 1.44×10^{-6}M, $[Pr^i\cdot]$ had decreased to 1.18 % 10^{-6}M, and the 'dimer' first appeared. The dimer concentration increased at the expense of the other radicals as the alkyne concentration was increased.

We have based a kinetic analysis (see *e.g.*, refs. 14 and 15) on the occurrence of reactions (2)—(7) (with R = CO_2H), in the concentration range of [RC≡CR] for which reaction (8) is not significant.

$$Ti^{III} + H_2O_2 \xrightarrow{k_{\text{In}}} Ti^{IV} + HO\cdot + OH^- \qquad (2)$$

$$HO\cdot + Pr^i{}_2SO \xrightarrow{k_3} Pr^i\cdot + Pr^iSO_2H \qquad (3)$$

$$Pr^i\cdot + RC{\equiv}CR \xrightarrow{k_4} Pr^iRC{=}CR\cdot \qquad (4)$$

$$\left.\begin{array}{rl} Pr^i\cdot + Pr^i\cdot \xrightarrow{k_5} & (5) \\ Pr^i\cdot + Pr^iRC{=}CR\cdot \xrightarrow{k_6} & (6) \\ 2Pr^iRC{=}CR\cdot \longrightarrow & (7) \end{array}\right\} \text{molecular products}$$

$$Pr^iRC{=}CR\cdot + RC{\equiv}CR \longrightarrow Pr^iRC{=}CR{-}CR{=}CR\cdot \qquad (8)$$

Steady-state analysis for the concentrations of the first formed vinyl radical and $Pr^i\cdot$ under conditions where the latter is significantly greater than the former [so that decay of the vinyl *via* reaction (7) can be neglected], leads to equations (9) [and hence 10] and (11), respectively.[14-16]

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* *Note added in proof:* These observations are in excellent agreement with the e.s.r. spectra for (18) reported after the submission of this manuscript (D. Griller, K. U. Ingold, and J. C. Walton, *J. Amer. Chem. Soc.*, 1979, **101**, 758; R. Sustman and H. Schmidt, *Chem. Ber.*, 1979, **112**, 1440).

† Concentrations of reagents are those after mixing. Under these conditions the excess of $Pr^i{}_2SO$ is such that ·OH radicals are completely scavenged by the sulphoxide (see ref. 14).

In accord with expectation based on equation (10), for low values of [RC≡CR] the increase in [Pr^{i}RC=CR$\cdot$] with alkyne concentration was found to be approximately linear. With [Pr^{i}RC=CR$\cdot$] as 0.59×10^{-6}M for [RC≡CR] 0.001 1M, and taking k_6 as *ca.* 2×10^{9} dm^3

$$k_4[\mathrm{Pr^i\cdot}][\mathrm{RC{\equiv}CR}] = k_6[\mathrm{Pr^i\cdot}][\mathrm{Pr^iRC{=}CR\cdot}] \qquad (9)$$

$$k_4 = k_6\,\frac{[\mathrm{Pr^iRC{=}CR\cdot}]}{[\mathrm{RC{\equiv}CR}]} \qquad (10)$$

$$k_{\mathrm{in}}[\mathrm{Ti^{III}}]_t[\mathrm{H_2O_2}]_t = k_4[\mathrm{Pr^i\cdot}][\mathrm{RC{\equiv}CR}] + 2k_5[\mathrm{Pr^i\cdot}]^2 \qquad (11)$$

mol^{-1} s^{-1} (a value typical of those found[17] for the termination of small aliphatic radicals), the rate constant for addition (k_4) is calculated as 1.1×10^{6} dm^3 mol^{-1} s^{-1}.

Analysis can also be based on the dependence of [Pr$^{i}\cdot$] on [RC≡CR]. Thus, from equation (11) the concentration of Pr$^{i}\cdot$ can be expressed as equation (12).

$$[\mathrm{Pr^i\cdot}] = -\frac{k_4[\mathrm{RC{\equiv}CR}]}{4k_5} \pm \frac{\sqrt{k_4{}^2[\mathrm{RC{\equiv}CR}]^2 + 8k_5k_{\mathrm{in}}[\mathrm{H_2O_2}]_t[\mathrm{Ti^{III}}]_t}}{4k_5} \qquad (12)$$

At low alkyne concentrations, such that $k_4{}^2[\mathrm{RC{\equiv}CR}]^2 \leqslant 8k_5k_{\mathrm{in}}[\mathrm{H_2O_2}]_t[\mathrm{Ti^{III}}]_t$, and taking the positive sign before the square root, this equation is simplified to (13). Thus a plot of [Pr$^{i}\cdot$] *versus* [RC≡CR] should

$$[\mathrm{Pr^i\cdot}] = -\frac{k_4[\mathrm{RC{\equiv}CR}]}{4k_5} + \sqrt{\frac{k_{\mathrm{in}}[\mathrm{H_2O_2}]_t[\mathrm{Ti^{III}}]_t}{2k_5}} \qquad (13)$$

be a straight line with slope $-k_4/4k_5$ and intercept $[\mathrm{Pr^i\cdot}]_0$ (for [RC≡CR] zero) of $\sqrt{k_{\mathrm{in}}[\mathrm{H_2O_2}]_t[\mathrm{Ti}]_t/2k_5}$ {*i.e.*, the value for [Pr$^{i}\cdot$] calculated from equations (2), (3), and (5), with no contribution from the other decay mode involving addition to alkyne}. Our results at low alkyne concentrations are in agreement with this; from the slope of the plot and taking $2k_5$ for Pr$^{i}\cdot$ as 2×10^{9} dm^3 mol^{-1} s^{-1} we calculate k_4 as 3.3×10^{6} dm^3 mol^{-1} s^{-1}, in reasonable agreement with the value derived from the appearance of the signal from Pr^{i}RC=CR$\cdot$. Although a kinetic analysis for the further reaction of the first formed vinyl radical with more alkyne is not feasible, it seems likely that the rate of the addition of Pr^{i}RC=CR$\cdot$ to RC≡CR (R = $\mathrm{CO_2H}$) is also of the order of 2×10^{6} dm^3 mol^{-1} s^{-1} (*cf.* values of 8.8×10^{6} and 5×10^{6} dm^3 mol^{-1} s^{-1}, respectively, for the addition of HOCH=CH$\cdot$ to HC≡CH and of HOCH=CH–CH=CH$\cdot$ to more acetylene[18]). If the rate constant for the second-order reaction of a first formed vinyl radical with more alkyne under our conditions is *ca.* 2×10^{6} dm^3 mol^{-1} s^{-1} then in cases where a rapid 1,5-shift precludes the detection of the vinyl radical [*cf.* Scheme 1], the rate constant for the intramolecular reaction must be at least 10^{6} s^{-1}.

EXPERIMENTAL

Details of the e.s.r. spectrometers and of the measurement and calibration of spectra have been described previously.[1] In most experiments a peristaltic pump was employed to pull solutions through a Varian two-way quartz mixing-chamber and cell. One stream typically contained titanium trichloride (10 ml of a 12.5% w/v solution dm^{-3}, 0.008M) and the substrate and the other stream hydrogen peroxide (8 ml of a 30% w/v solution dm^{-3}, 0.08M). For experiments in acid solution, concentrated sulphuric acid was added to the titanium(III)-containing stream, whereas for experiments at high pH the titanium ions were sequestered with the disodium salt of ethylenediaminetetra-acetic acid (6 g dm^{-3}, 0.016M) and the pH adjusted with potassium carbonate; pH values were varied between 1 and 2 and between 7 and 9, respectively, in order to achieve optimum resolution of the spectra. Concentrations of butynedioic acid employed are described in the text.

In the experiment involving the addition of isopropyl radicals to butynedioic acid, a three-way modified flow system was employed, together with a peristaltic pump. Relative radical concentrations were obtained from measurements of peak amplitudes and linewidths, and the absolute concentration of Pr$^{i}\cdot$ in the absence of butynedioic acid was obtained by comparison with the signal from a standard solution of vanadyl sulphate.[19] The mixing time (*ca.* 50 ms) applicable to the flow system and flow rate employed was determined from the variation in [$\cdot\mathrm{CH_2CMe_2OH}$] with $[\mathrm{H_2O_2}]_0$ in a series of experiments with Ti$^{\mathrm{III}}$, $\mathrm{H_2O_2}$, and $\mathrm{Me_3COH}$, as indicated previously.[16]

Sulphoxides,[2] diazonium salts,[3] 1,3-dioxolans,[20] and mixed ethers[21] were prepared by methods reported previously; all other reagents employed were commercial samples, used without further purification.

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