An Electron Spin Resonance Study of Pentenynyl and Pentadiynyl Radicals

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Pent-2-en-4-ynyl radicals were generated from pent-1-en-4-yne and *cis*- and *trans*-1-bromopent-2-en-4-yne and observed in the *trans* (4) and *cis* (5) conformations by e.s.r. spectroscopy. The rate constant for the isomerization (5) $\longrightarrow$ (4) was determined by kinetic e.s.r. to be given by equation (i) and for the isomerization (4) $\longrightarrow$ (5) the

$$\log k_1 = (13.2 \pm 1.3) - (47.5 \pm 8.0 \text{ kJ mol}^{-1}/2.3RT)\ \text{s}^{-1} \qquad \text{(i)}$$

rate constant was found to be given by equation (ii). From the observed barriers to rotation the methane based

$$\log k_{-1} = (13.0 \pm 1.3) - (49.2 \pm 8.0 \text{ kJ mol}^{-1}/2.3RT)\ \text{s}^{-1} \qquad \text{(ii)}$$

stabilization energies of (4) and (5) were estimated to be 112 and 110 kJ mol^{-1}. E.s.r. spectra were also recorded for the 1-trimethylsiloxy-derivatives of (4) and (5), pent-2-en-4-ynyl radicals, 1-trimethylsiloxypent-2-en-4-ynyl radicals, and penta-1,4-diynyl radicals. The enthalpies of formation, structures, and stabilization energies of the hydrocarbon radicals were computed using the MINDO/3 method. The conformational interconversion of radicals (4) and (5) was also examined by MINDO/3.

IT was shown recently that pentadienyl radicals can exist in two planar conformations (1) and (2).[1,2] Radical (2) converts into (1) at temperatures above *ca.* 210 K but,

(1)

(2)

unexpectedly, radical (1) does not convert into (2) at temperatures up to at least 420 K. Another hydrocarbon radical which is potentially capable of existing in two planar conformations is pent-2-en-4-ynyl (3). We have observed the two conformations of this radical and explored the thermodynamic relationship between them by e.s.r. spectroscopy. We have also generated pent-2-en-4-ynyl radicals, trimethylsiloxy-derivatives of both types of radical, and penta-1,4-diynyl radicals to extend our knowledge of this kind of delocalised system. A study of the structures and electron distributions in these radicals by SCF-MO methods is also reported.

RESULTS AND DISCUSSION

Pent-2-en-4-ynyl Radicals.—Pent-1-en-4-yne (3) was first made by Grignard and his co-workers from allyl bromide and ethynylmagnesium bromide.[3] Subsequent attempts to use this method were not successful until it was discovered that small amounts of copper(I) chloride were needed to catalyse the reaction.[4] We found that good yields of pent-1-en-4-yne can be obtained using the copper(I) chloride method with THF as solvent.

The photochemical reaction of bromotrichloromethane with this enyne resulted in the formation of $CCl_3CH_2CHBrCH_2C{\equiv}CH$ by addition of $CCl_3\cdot$ radicals to the double bond, and hydrogen abstraction was minor. However, t-butoxyl radicals preferentially abstract hydrogen from C(3) and when a solution of (3) and di-t-butyl peroxide in cyclopropane was photolysed in the cavity of an e.s.r. spectrometer the spectrum shown in Figure 1 was obtained at low temperatures. The spectrum can readily be analysed in terms of five non-equivalent hydrogen atoms and it clearly belongs to pent-2-en-4-ynyl radicals in one or other of the two possible conformations. Even at the lowest temperature reached (135 K) traces of a second radical were visible, and as the temperature was raised the proportion of the second radical increased. The second radical also showed hyperfine coupling to five non-equivalent hydrogens, indicating that it was the second conformation of the pent-2-en-4-ynyl radical.

FIGURE 1 E.s.r. spectrum of *cis*-pent-2-en-4-ynyl radicals (5) at 9.51 GHz. Radicals generated from pent-1-en-4-yne in cyclopropane at 145 K. Traces of the *trans*-radical (4) can be seen just upfield from the third line on the left and downfield from the corresponding line on the right

The relative concentrations of the two species were measured over a range of temperatures, neat di-t-butyl peroxide being used as solvent for temperatures greater than *ca.* 280 K, and the results are shown in Figure 2. In the range 135—220 K the first radical, which was later shown to be (5) (see below), predominated, but the amount of (4) steadily increased. The two radicals are formed by hydrogen abstraction from the conformers of pent-1-en-4-yne, *i.e.* (3a and b) (see Scheme). In this temperature range the rate of abstraction leading to (5) must be greater than the rate leading to (4), but as the temperature increases the two rates approach each other. In the range 230—260 K there is a steep increase in the relative amount of (4) which suggests that (5) is converting into (4) at these temperatures. Above 270 K the

[(4)] : [(5)] concentration ratio reaches a constant value of *ca.* 1.9. This suggests that here both radicals can interconvert and equilibrium is set up.

In order to show which e.s.r. spectrum corresponded to which conformation of the pent-2-en-4-ynyl radical and in order to determine if conversion of one conformer to the other really occurs, it was necessary to generate the radicals from a precursor which would yield specifically (4) [or (5)] initially. *trans*-Pent-2-en-4-yn-1-ol was prepared from sodium acetylide and epichlorohydrin [5] and a mixture of *cis*- and *trans*-enynols was obtained by using lithium acetylide.[6] *trans*-1-Bromopent-2-en-4-yne (6) was made by converting the *trans*-alcohol to the mesylate which was then stirred with lithium bromide. A mixture of *cis*- and *trans*-bromides was made by treatment of the *cis*–*trans*-alcohol mixture in the same way, and pure (7) was then separated by preparative g.l.c.

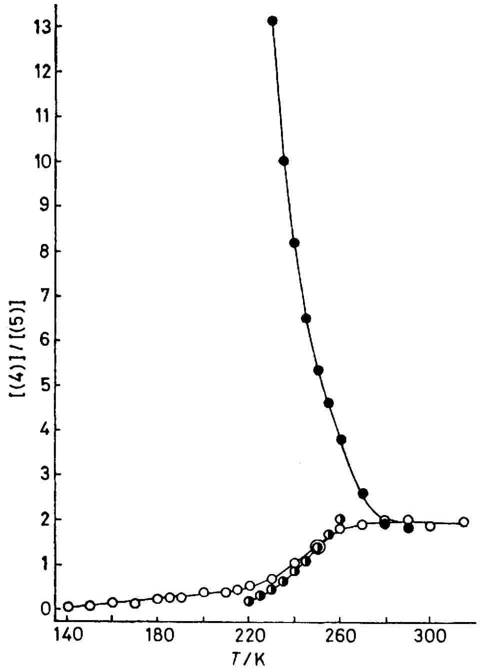
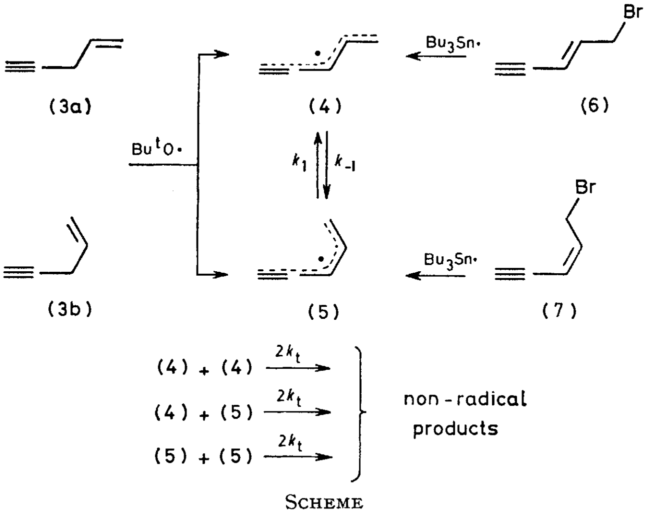


FIGURE 2 Temperature dependence of the ratio of the concentration of *trans*-(4) and *cis*-pent-2-en-4-ynyl radicals (5). Filled circles, *trans*-1-bromopent-2-en-4-yne as precursor. Half-filled circles, *cis*-1-bromopent-2-en-4-yne as precursor. Open circles, pent-1-en-4-yne as precursor



SCHEME

An e.s.r. spectrum of pent-2-en-4-ynyl in the *cis*-conformation (5), was obtained by photolysis of a mixture of the *cis*-bromoenyne (7) and hexa-n-butylditin in isopentane solution; triethylsilyl radicals were equally effective. The *cis*-radical (5) was the only radical observed in the temperature range 150—220 K and the spectrum was the same as that shown in Figure 1. At temperatures above 220 K the *trans*-radical (4) appeared. The concentration ratio [(4)] : [(5)] as a function of temperature is shown in Figure 2. This enabled the *cis*-conformer to be definitely identified and showed that the *cis*-form (5) converts into the *trans*-form (4) at >220 K.

The e.s.r. spectrum of *trans*-pent-2-en-4-ynyl (4) was obtained by similar treatment of the *trans*-bromide (6). The *trans*-radical (4) was the only radical observed in the temperature range 150—230 K and the spectrum is shown in Figure 3. The e.s.r. parameters of the two radical conformers are listed in Table 2. At higher temperatures the e.s.r. spectrum of the *cis*-radical (5) began to appear. The temperature dependence of the [(4)] : [(5)] ratio from this precursor is also shown in Figure 2. This indicates that the *trans*-radical converts to the *cis*-radical at >230 K. The behaviour of pent-2-en-4-ynyl radicals parallels that of pentadienyl radicals, except that for the latter no *trans* to *cis* conversion takes place in the accessible temperature range.[1,7]

FIGURE 3 E.s.r. spectrum of *trans*-pent-2-en-4-ynyl radicals (4) at 9.49 GHz. Radicals generated from *trans*-1-bromopent-2-en-4-yne at 175 K

The kinetics of the *trans* (4) to *cis* (5) interconversion was investigated by determining the absolute concentrations of the two radicals in the temperature range 230—260 K when they were generated from each of the *trans* (6) and *cis* (7) bromides. The standard e.s.r. method [8] was used and the results are given in Table 1.

The bromides themselves, (6) and (7), were found to isomerise during g.l.c. analysis, if the column was operated at temperatures above *ca.* 100 °C (see Experimental section). It seemed possible therefore that isomerization of the reactants (6) and (7) might occur under the e.s.r. conditions used in the kinetic experiments. At the end of the reactions the e.s.r. tubes were therefore opened and the contents examined by g.l.c. It was found that in the reaction of (6) the bromide remaining at the end was unchanged and no (7) could be detected. Similarly no (6) could be detected after the photochemical reaction involving (7).

TABLE 1

Kinetics of the isomerization of *cis*- and *trans*-pent-2-en-4-ynyl radicals

	cis-Bromide (7)		*trans*-Bromide (6)			
T/K	10^8[(5)]/ mol dm^{-3}	10^8[(4)]/ mol dm^{-3}	10^8[(5)]/ mol dm^{-3}	10^8[(4)]/ mol dm^{-3}	$10^8k_{-1}/2k_\mathrm{t}$/ mol dm^{-3}	$10^8k_1/2k_\mathrm{t}$/ mol dm^{-3}
230	4.31	2.00	0.67	8.88	3.4	1.0
235	3.82	2.49	0.84	8.43	5.0	1.4
240	3.20	2.84	0.98	7.95	7.1	2.0
245	2.75	3.06	1.15	7.50	9.6	2.8
250	2.31	3.29	1.29	7.02	13.8	4.1
255	2.00	3.42	1.42	6.53	19.4	5.9
260	1.69	3.60	1.60	6.08	35.4	11.3

Figure 2 shows that the *cis*-radical (5) begins to convert into (4) at lower temperatures than the *trans*-radical (4) converts into (5). If the back reaction (4) ⟶ (5) can be neglected in a particular temperature range then application of the steady state approximation leads to equation (A).[8] Unfortunately, even at the lowest

$$k_1/2k_\mathrm{t} = \{[(4)]^2/[(5)]\} + [(4)] \qquad \text{(A)}$$

temperatures where the two radicals could be detected, the (4) ⟶ (5) isomerization was significant and the use of (A) leads to a curved Arrhenius type plot. Application of the steady state approximation to the mechanism given in the Scheme, including reversible isomerization of the two pent-2-en-4-ynyl radicals and taking the *cis*-bromide (7) as the reactant from which they are generated leads to equation (B). The rate constants for

$$k_1/2k_\mathrm{t} - k_{-1}/2k_\mathrm{t}\{(4)/[(5)]\} - [(4)]^2/[(5)] - [(4)] = 0 \qquad \text{(B)}$$

termination reactions involving (4) and (5) have been assumed equal, since the termination rates will be diffusion controlled. This equation reduces to equation (A) when k_{-1} is negligible. In principle the two rate constant ratios could be obtained by carrying out experiments at different light intensities and plotting the measured quantities $\{[(4)]^2/[(5)] + [(4)]\}$ against $\{[(4)]/[(5)]\}$; the gradient and intercept would then give $k_{-1}/2k_\mathrm{t}$ and $k_1/2k_\mathrm{t}$. In the present case the signal heights at full light intensity were too small to make this a practical proposition. When the radicals are generated from the *trans*-bromide (6) a second equation (C) may be derived.

$$k_{1-}/2k_\mathrm{t} - k_1/2k_\mathrm{t}\{[(5)]/[(4)]\} - [(5)]^2/[(4)] - [(5)] = 0 \qquad \text{(C)}$$

Equations (B) and (C) can therefore be solved as a pair of simultaneous equations using the radical concentrations from each bromide given in Table 1. The rate constant ratios derived in this way are in the last two columns of Table 1. Least squares analysis of the data leads to the Arrhenius parameters of equations (D) and (E) where the error limits have been estimated from the scatter on the graphs. The rate constant for termination of n-pentyl radicals, which are a reasonable model for pent-2-en-4-ynyl radicals, was reported to be given by equation (F).[9] The rate constant for isomerization

$$\log(k_1/2k_\mathrm{t}) = (0.88 \pm 0.6) - (36.9 \pm 5.0\ \mathrm{kJ\ mol^{-1}}/2.3RT)\ \mathrm{mol\ dm^{-3}} \qquad \text{(D)}$$

$$\log(k_{-1}/2k_\mathrm{t}) = (0.74 \pm 0.6) - (38.6 \pm 5.0\ \mathrm{kJ\ mol^{-1}}/2.3RT)\ \mathrm{mol\ dm^{-3}} \qquad \text{(E)}$$

$$\log 2k_\mathrm{t} = (12.30 \pm 0.7) - (10.6 \pm 3.0\ \mathrm{kJ\ mol^{-1}}/2.3RT)\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \qquad \text{(F)}$$

of *cis*-(5) to *trans*-(4) is therefore given by equation (G)

$$\log k_1 = (13.18 \pm 1.3) - (47.5 \pm 8.0\ \mathrm{kJ\ mol^{-1}}/2.3RT)\ \mathrm{s^{-1}} \qquad \text{(G)}$$

and the rate constant for isomerization of *trans*-(4) to *cis*-(5) is given by (H).

$$\log k_{-1} = (13.04 \pm 1.3) - (49.2 \pm 8.0\ \mathrm{kJ\ mol^{-1}}/2.3RT)\ \mathrm{s^{-1}} \qquad \text{(H)}$$

The *A* factors are normal for unimolecular reactions of this type. The activation energy for isomerization of the *cis*-radical (5) is *ca.* 10 kJ mol^{-1} higher than the activation energy for isomerization of *cis*-pentadienyl radicals (2) which was estimated to be 37 kJ mol^{-1}.[7] The activation energy for isomerization of the *trans*-radical (4) is much *lower* than that for the analogous isomerization of the *trans*-pentadienyl radical (1).

The difference in the two activation energies for the isomerizations of (5) and (4), *i.e.* ΔH −1.7 kJ mol^{-1}, gives the enthalpy difference between the two radical conformers. At temperatures above about 280 K the two radicals are in equilibrium [relationships (I)] and the

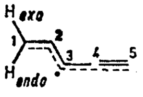
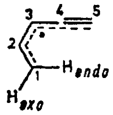
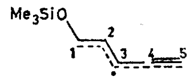
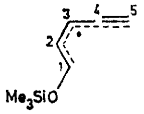
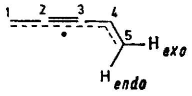
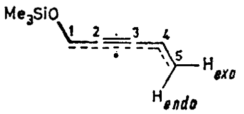
$$(5) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (4 \quad \frac{k_{-1}}{k_1} = \frac{[(4)]}{[(5)]} = K \qquad \text{(I)}$$

equilibrium constant K at 298 K is 1.9 ± 0.1 as determined from the radical concentrations shown in Figure 2. From this ΔG° for the equilibrium is calculated to be -1.6 ± 0.1 kJ mol^{-1}. The entropy difference between (4) and (5) must be extremely small so that $\Delta G^\circ \sim \Delta H^\circ$ and it is seen that there is excellent agreement between the ΔH values calculated from the kinetic experiments and from the equilibrium constant. The ΔH° value for the radical isomerization also compares well with the known experimental difference in the heats of formation of the hydrocarbons, *cis*- and *trans*-pent-2-en-4-yne, *i.e.*[10] −1.3 kJ mol^{-1}.

The e.s.r. spectrum of the *trans*-1-trimethylsiloxypent-2-en-4-ynyl radical (8) was obtained by photolysis of a mixture of the corresponding silyl ether and di-t-butyl peroxide in isopentane. The e.s.r. parameters are recorded in Table 2. No indication of the *cis*-radical (9) was obtained in this solvent. The system was examined at higher temperatures in neat di-t-butyl peroxide and there was slight evidence of the presence of the *cis*-conformer (9) at 310 K, although the spectrum was too weak to allow definite identification. Pure *cis*-silyl ether could not be obtained, but the spectrum of the *cis*-radical (9) was observed together with that of the *trans*-conformer (8) on photolysis of a mixture of the *cis*- and *trans*-silyl ethers. The e.s.r. parameters are given in Table 2.

TABLE 2

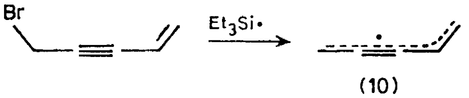
E.s.r. parameters of pentenynyl and pentadiynyl radicals[a]

Radical	T/K	g-Factor	a/mT	
 (4)	175	2.0025	H(1*endo*)	1.06
			H(1*exo*)	1.15
			H(2)	0.36[b]
			H(3)	1.38
			H(5)	0.84
 (5)	150	2.0025	H(1*endo*)	1.08
			H(1*exo*)	1.15
			H(2)	0.35[c]
			H(3)	1.45
			H(5)	0.72
 (8)	210	2.0029	H(1)	1.11
			H(2)	0.28[d]
			H(3)	1.32
			H(5)	0.76
 (9)	220	2.0029	H(1)	1.09
			H(2)	0.31
			H(3)	1.40
			H(5)	0.67
 (10)	200	2.0026	2H(1)	1.54
			H(4)	0.41[e]
			H(5*endo*)	0.67
			H(5*exo*)	0.70
 (11)	200	2.0027	H(1)	1.35[f]
			H(4)	0.36[g]
			H(5*endo*)	0.65[h]
			H(5*exo*)	0.68[i]
 (13)	160	2.0028	H(1,5)	0.95
			H(3)	1.66

[a] Hyperfine splittings assigned to specific hydrogens by analogy with allyl,[12] pentadienyl,[7] and propargyl radicals. [b] $\partial a/\partial T$ = 0.12 μT/K. [c] $\partial a/\partial T$ = 0.16 μT/K. [d] $\partial a/\partial T$ = 0.17 μT/K. [e] $\partial a/\partial T$ = 0.30 μT/K. [f] $\partial a/\partial T$ = −0.60 μT/K. [g] $\partial a/\partial T$ = 0.37 μT/K. [h] $\partial a/\partial T$ = 0.19 μT/K. [i] $\partial a/\partial T$ = −0.20 μT/K.

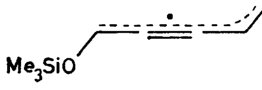
The hyperfine splittings of hydrogens attached to C(1)—C(3) in radicals (4) and (5) are significantly larger than those of similarly placed hydrogens in the pentadienyl radicals (1) and (2).[1,2] The hyperfine splittings of the analogous hydrogens in trimethylsilyl-substituted radical (8) are also larger than those of their counterparts in the substituted pentadienyl radical.[7] This indicates that spin density is less readily delocalised over the triple bond than it is over the double bond.

Pent-2-yn-4-enyl and Penta-1,4-diynyl Radicals.—Pent-2-yn-4-en-1-ol was synthesised from vinyl bromide and propargyl alcohol[11] and then converted into 1-bromopent-2-yn-4-ene by treatment of the mesylate with lithium bromide. Pent-2-yn-4-enyl radicals (10) were generated by photolysis of a solution of the bromide, triethylsilane and di-t-butyl peroxide in cyclopropane. The e.s.r. parameters of the resulting radical (10) are recorded in Table 2. There is only one possible conformation of this radical, and, as expected, no changes in the e.s.r. spectrum were observed at different temperatures, apart from a small variation in the hyperfine splitting due to H(4) (see Table 2). Photolysis of a solution of the trimethylsilyl ether from pent-2-yn-4-en-1-ol and di-t-butyl peroxide in cyclopropane generated the corresponding trimethylsiloxy-substituted radical (11), and the e.s.r. parameters are given in Table 2. There are two possible conformations of this radical, *i.e.* (11a and b).

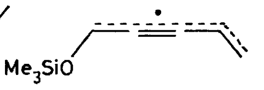


(10)

The difference in the environments of the vinyl hydrogens is very slight and it is doubtful if distinctly different spectra would be obtained from these two species. In practice only one spectrum, without visual evidence of line broadening, was observed throughout the whole accessible temperature range, but *all* the hyperfine splitting showed apparent temperature variation (see Table 2). One possible explanation of this anomalous behaviour is that the spectrum actually consisted of two closely overlapping spectra due to the two conformations (11a and b). As the temperature was varied the proportions of the two radicals changed and this led to *apparent* temperature variations in the hyperfine splittings.



(11a)

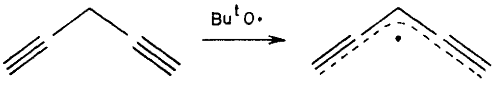


(11b)

The hyperfine splittings of hydrogens at C(5) in both radicals (10) and (11) are considerably smaller than the hyperfine splittings of terminal hydrogens in pentadienyl radicals. At the same time the hyperfine splittings of the hydrogens at C(1) in the pent-2-yn-4-enyl radicals are larger than their counterparts in the pentadienyl radicals. This confirms the idea that spin density is transmitted less readily by triple than by double bonds.

The hydrogens at C(4) in radicals (10) and (11) and those at C(2) in radicals (4), (5), (8), and (probably) (9) all have hyperfine splittings which are similar in magnitude to the analogous hydrogens in pentadienyl[1] and allyl.[12] Similarly, these hyperfine splittings all show positive temperature coefficients. This temperature coefficient indicates that there is appreciable torsional motion about the adjacent C–Cbonds. It arises because additional positive spin reaches H(2) or H(4) by hyperconjugation when the vinyl group to which they are attached is twisted out of the radical plane. The sign and magnitude of the temperature coefficient give a good indication that a[H(2)] and a[H(4)] are positive coupling constants.

Penta-1,4-diynyl radicals (13) were generated by hydrogen abstraction from penta-1,4-diyne (12) by t-butoxyl radicals. The pure diyne (12) decomposes in



(12) (13)

only a few minutes[13] and therefore it was transferred rapidly by syringe from the cooled trap used to collect it from the preparative g.l.c. instrument into a cooled e.s.r. tube. Cyclopropane solvent and di-t-butyl peroxide were added and the e.s.r. spectra run rapidly. Good spectra were obtained at 235 K and above, but at lower temperatures some diyne crystallised out and only weak signals were observed. The spectrum consisted of a double triplet and the e.s.r. parameters of the radical, which were essentially independent of temperature, are given in Table 2. The 1.66 mT hyperfine splitting from H(3) in (13) is large compared to a[H(3)] from pentadienyl radicals, and this again suggests relatively poor delocalization of spin density in the diynyl system.

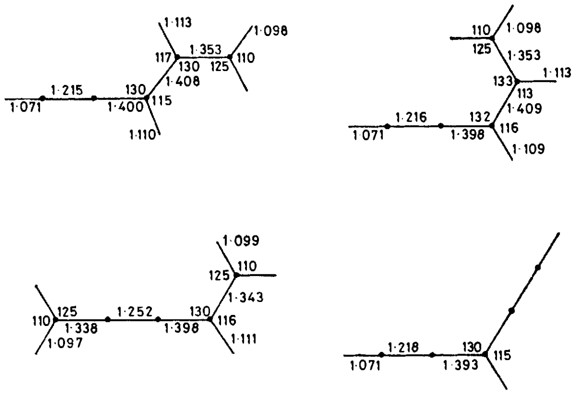


FIGURE 4 Structures of pentenynyl and pentadiynyl radicals calculated by MINDO/3

MO Study using the MINDO/3 Method.—The structures and enthalpies of formation of the hydrocarbon radicals were calculated using the MINDO/3 program.[14,15] Geometries were fully optimised with respect to all bond lengths, bond angles, and dihedral angles. The calculated structures, all of which were essentially planar, are shown in Figure 4. The C–C bond lengths, single, double, and triple, are little changed from their values in the saturated hydrocarbon precursors. The calculations thus support the conclusion derived from the e.s.r.

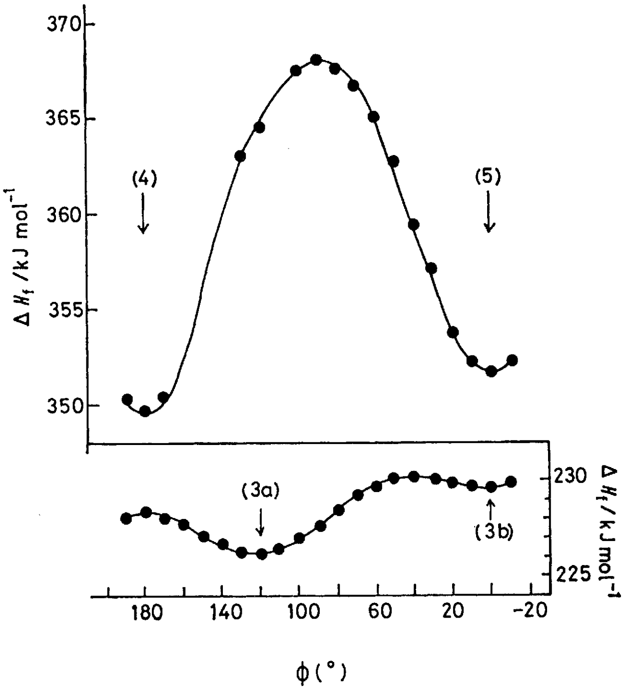


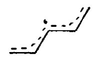
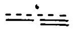
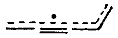
FIGURE 5 MINDO/3 calculations of the enthalpies of formation of the conformers of pent-1-en-4-yne and pent-2-en-4-ynyl radicals as a function of the dihedral angle ϕ about the C(2)–C(3) bond. Lower box, pent-1-en-4-yne. Upper box, pent-2-en-4-ynyl radicals

spectra, that triple bonds are less effective at delocalising unpaired spin.

The conformations of pent-1-en-4-yne were studied by varying the dihedral angle (ϕ) about the C(2)–C(3) bond with complete optimization with respect to all other bond lengths and angles. The variation in the enthalpy of formation with ϕ is shown in Figure 5. MINDO/3 predicts two stable conformations for pent-1-en-4-yne, an *s-trans* form at ϕ 120°, which is only slightly more stable than an *s-cis* form at ϕ 0, in which all five carbon atoms are planar. The conformations of the pent-2-en-4-ynyl radicals were studied in a similar way and the results are also plotted in Figure 5. The two minima at ϕ 180° and 0° correspond to the *trans*- (4) and the *cis*- (5) radicals respectively. MINDO/3 predicts (4) to be lower in energy by 2.0 kJ mol^{-1}, and this compares very well with the experimental $\Delta H°$ values. It is seen in Figure 5 that hydrogen abstraction from the *s-cis*-conformer of pent-1-en-4-yne will give the *cis*-radical (5) with very little readjustment of the molecule, because all five carbon atoms are already planar. On the other hand hydrogen abstraction from the *s-trans*-conformer will produce radical (4) only after rotation about the C(2)–C(3) bond by about 60°. This may make hydrogen abstraction from the *s-cis*-conformer more favourable. A steric factor may also favour hydrogen-abstraction from the *s-cis*-conformer since the two hydrogens at C(3) are slightly less shielded by the terminal hydrogens of the vinyl group than they are in the *s-trans*-conformer. The preponderance of the *cis*-radical (5) at low temperatures observed by e.s.r. would then result from a combination of these two factors.

TABLE 3

Enthalpies of formation and stabilization energies of delocalised radicals [a]

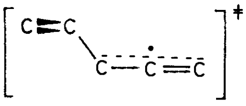
Radical	$\Delta H_f°$ gp. cont.	$\Delta H_f°$ MINDO/3	E_s^{MeH} [b] Thermochem.	E_s^{MeH} E.s.r.	E_s^{MeH} MINDO/3
	159	184	67	⩾70 [c]	61 [e]
	220	228	101	104 [d]	70
	216	224		⩾130 [d]	73 [e]
		322	63		42
		338			38
	400	352		110	69
	396	350		112	68
		478			85

[a] All in kJ mol^{-1}. [b] Methane based stabilization (resonance) energies from thermochemical determination of the relevant bond dissociation energies (see text). [c] See ref. 12. [d] From ref. 7. [e] These values are essentially the same as the resonance energies calculated by Dewar *et al.*[18] also using MINDO/3.

The calculated enthalpies of activation for isomerization of *cis* (5) to *trans* (4) *i.e.*, E_1, and for the reverse process, *i.e.* E_{-1}, were found to be 16.3 and 18.3 kJ mol^{-1}, respectively. Although these calculated values are considerably less than the experimental activation energies (47.5 and 49.2 kJ mol^{-1}, see above) the MINDO/3 method deserves respect for having calculated from first principles to within a factor of two or three of the true result. Apparently MINDO/3 consistently underestimates activation energies for this type of isomerization since the barriers to bond rotation in allyl[14] and pentadienyl are also underestimated.

The MINDO/3 calculated enthalpies of formation ($\Delta H_f°$) of a number of delocalised hydrocarbon radicals are given in Table 3. Agreement between the MINDO/3 values and those derived by the group contributions (g.c.) method[16] (column 2 of Table 3) is satisfactory except for pent-2-en-4-ynyl radicals. Either the MINDO/3 or the g.c. results could be in error.

In the transition state (14) for the (4) ⟶ (5) isomerization the unpaired electron is confined to the propargyl moiety of the pent-2-en-4-ynyl system. The stabilization energy (E_s) for *trans*- and *cis*-pent-2-en-4-ynyl radicals can therefore be considered to equal the sum of the energy associated with the barrier to rotation, plus the propargyl stabilization energy. E_s(propargyl) was recently found to be 38.4 kJ mol^{-1}, as determined from the difference in the primary C–H bond strengths in propane and propyne.[17] Stabilization (resonance) energies of odd conjugated systems are best defined with respect to methyl radicals as the reference species;[9,18] they are then called 'methane based' stabilization energies E_s^{MeH}. The methane based stabilization energy of propargyl radicals is therefore 63 kJ mol^{-1}. Combining this with the barriers to rotation in *trans* (4) and *cis* (5) measured by kinetic e.s.r. spectroscopy gives the E_s^{MeH} values listed in Table 3. The stabilization energies of a number of delocalised radicals are compared in Table 3, which also lists E_s^{MeH} values derived from the MINDO/3 enthalpies of formation of the radicals R· and their hydrocarbon precursors RH.


(14)

A reasonably coherent picture emerges from the data in Table 3. The stabilization energies of *cis*- and *trans*-pent-2-en-4-ynyl radicals are somewhat less than the sum of the E_s^{MeH} values of allyl and propargyl. Similarly, E_s^{MeH} for *cis*-pentadienyl radicals is less than twice the allyl value. The E_s^{MeH} for *trans*-pentadienyl radicals may also be less than twice the allyl value, but the experimental evidence is lacking. The MINDO/3 E_s^{MeH} values are generally less than the experimental results, but they also show this same effect. The propargyl stabilization energy is predicted to be less than that of allyl and the pentenynyl radicals are predicted to have lower E_s^{MeH} than the pentadienyl radicals. The MINDO/3 result for penta-1,4-diynyl radicals is, however, anomalously high.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian HA-100 and/or Bruker WP 80 instruments for CCl_4 solutions at ambient temperature with tetramethylsilane as internal standard. The ^{13}C n.m.r. spectra were recorded on a Varian CFT 20 spectrometer. Mass spectra were obtained with an A.E.I. MS 902 spectrometer. G.l.c. analyses were carried out on a Pye 105 instrument with glass columns packed with Embaphase silicone oil, tritolyl phosphate, or ββ'-oxydipropiononitrile on Chromosorb G as solid support. E.s.r. spectra were recorded with a Bruker ER 200D spectrometer.

Commercial di-t-butyl peroxide was passed through a column of alumina and then distilled *in vacuo*. Hexa-n-butylditin was obtained commercially, distilled *in vacuo*, and stored under nitrogen.

Pent-1-*en*-4-*yne* (3).—To ethynylmagnesium bromide[19] in THF prepared from magnesium (12 g) and ethyl bromide (60 g) was added copper(I) chloride (1 g). Then dried allyl bromide (30.2 g) was slowly added to the stirred solution. After the addition was complete (*ca.* 1 h) a second portion of copper(I) chloride (1 g) was added and an exothermic reaction set in. The solution was stirred for 16 h, then filtered through glass wool, washed four times with saturated salt solution, and dried ($MgSO_4$). The yellow liquid was rapidly distilled through a Vigreux column to give a clear solution of THF containing *ca.* 8% pent-1-en-4-yne. G.l.c. analysis showed the total yield to be 73 mol %. The solution was carefully distilled through a 15 cm column packed with glass helices, material boiling in the range 35—45 °C being collected. G.l.c. analysis showed this to contain 40% pent-1-en-4-yne. Pure material was obtained by preparative g.l.c. on a 7 ft column packed with 10% ββ'-oxydipropiononitrile operated at 50 °C, δ_H 1.95 (1 H, t, J 2 Hz), 2.9 (2 H, m), and 4.95—5.90 (3 H, m), δ_C 22.6 (t, J 24 Hz), 70.6 (d, J 49 Hz), 80.4(s), 116.2 (dd, J 23, 9 Hz), and 131.7 p.p.m. (d, J 21 Hz).

trans-1-*Bromopent*-2-*en*-4-*yne* (6).—*trans*-Pent-2-en-4-yn-1-ol[5] (4.0 g) and triethylamine (6.1 g) in dry dichloromethane (150 ml) were stirred under nitrogen and cooled in an ice–salt bath. Methanesulphonyl chloride (5.2 g) was added slowly over 15 min, and the mixture stirred for a further 20 min. Water was added, the dichloromethane layer separated, and then washed with 2M-HCl (200 ml), 5% brine (100 ml), and saturated $NaHCO_3$ (200 ml). The solution was dried (Na_2SO_4) and CH_2Cl_2 removed on a rotary evaporator. The resulting mesylate showed the characteristic bands in the i.r. spectrum at 1 340 and 1 170 cm^{-1}. It was added immediately to a solution of lithium bromide (10 g) in dry acetone (125 ml). A precipitate of lithium mesylate appeared immediately and the solution was refluxed for 0.5 h. The precipitate was filtered off and the acetone removed by distillation at atmospheric pressure through a Vigreux column. Water was added to the residual oil which was then extracted with ether. The ether layers were dried (Na_2SO_4) and the ether removed by atmospheric pressure distillation through a Vigreux column. The residue was then distilled under reduced pressure and gave product (3.4 g), b.p. 41—48° at 15 mmHg. The ^{1}H n.m.r. showed this to be a mixture of *trans*-1-bromopent-2-en-4-yne and mesityl oxide; the latter probably formed by base-catalysed condensation of the acetone. This side reaction of the solvent only seems to occur with compounds containing terminal acetylene groups. Pure *trans*-bromide was separated by preparative g.l.c. using a 7 ft column packed with 10% silicone oil. When the column was operated at temperatures greater than *ca.* 100 °C the bromide was found to isomerise to a mixture of *cis* + *trans*. A temperature of 70 °C gave pure *trans*-bromide, δ_H 3.05 (1 H, d, J 2.5 Hz), 4.08 (2 H, d, J 7 Hz), 5.8 (1 H, dd, J 14 3 Hz), and 6.25—6.7 (1 H, dt, J_t 7, J_d 16 Hz) (Found: M^+, 143.957 9. $C_5H_5{}^{79}Br$ requires M, 143.957 5). The ^{13}C n.m.r. spectrum is given in Table 4.

cis-1-*Bromopent*-2-*en*-4-*yne* (7).—A mixture of *cis*- and *trans*-pent-2-en-4-yn-1-ol[6] was converted to a mixture of the *cis*- and *trans*-bromides by the method described above for the *trans*-compound. Pure *cis*-bromide (7) was separated from *trans*-bromide and mesityl oxide by preparative g.l.c. on a 7 ft column packed with 10% silicone oil on Chromosorb G operated at 70 °C, m/e 146, 144 ($C_5H_5{}^{81}Br$), δ_H 3.26 (1 H, d, J 3 Hz), 4.20 (2 H, d, J 8 Hz), 5.6 (1 H, dd, J 3, 11 Hz), and 6.1—6.4 (1 H, dt, J_t 7, J_d 10 Hz). The ^{13}C n.m.r. spectrum is given in Table 4.

trans- *and* cis-1-*Trimethylsiloxypent*-2-*en*-4-*yne*.—*trans*-Pent-2-en-4-yn-1-ol (1.0 g) and pyridine (1.0 g) were stirred at room temperature in n-pentane (10 ml). Trimethylsilyl chloride (1.6 g) was added drop by drop. The solution was filtered, the n-pentane sucked off, and the residual oil distilled in a Vigreux flask to give *trans*-1-trimethylsiloxypent-2-en-4-yne (0.5 g), b.p. 59° at 18 mmHg, δ_H 0.15 (9 H, s), 2.75 (1 H, s), 3.90 (2 H, m), 5.25—5.45 (1 H, m), and 5.85—6.25 (1 H, m).

A mixture of the *trans*- and *cis*-trimethylsilyl ethers was made from the mixture of *trans*- and *cis*-pent-2-en-4-yn-1-ols by the same method. The ^{1}H n.m.r. of the *cis*-compound was deduced from the n.m.r. spectrum of the mixture and the known n.m.r. spectrum of the *trans*-isomer. ^{1}H N.m.r. of *cis*-isomer: δ_H 0.5 (9 H, s), 3.1 (1 H, s), 4.4 (2 H, m), 5.35—5.6 (1 H, m), and 5.9—6.3 (1 H, m). The ratio of *trans*- to *cis*-isomer was found to be 1.8 from the n.m.r. peak heights.

1-*Bromopent*-2-*yn*-4-*ene*.—Pent-2-yn-4-en-1-ol was made from vinyl bromide and propargyl alcohol by the method of Sonogashira *et al.*[11] The alcohol (4 g) was converted into the bromide by treatment of the mesylate with lithium bromide as described above. No mesityl oxide was formed in this case, and distillation in a Vigreux flask gave 1-*bromopent*-2-*yn*-4-*ene* (4.3 g, 60%), b.p. 57° at 33 mmHg (Found: M^+, 143.957 8. $C_5H_5{}^{79}Br$ requires M, 143.957 5), δ_H 4.1 (2 H, d, J 2 Hz) and 5.4—5.9 (3 H, m). See Table 4 for the ^{13}C n.m.r. spectrum.

1-*Trimethylsiloxypent*-2-*yn*-4-*ene*.—The silyl ether was made from pent-2-yn-4-en-1-ol by the method described above in 58% yield, b.p. 52° at 15 mmHg, δ_H 0.2 (9 H, s), 4.3 (2 H, s), and 5.2—5.8 (3 H, m).

TABLE 4

^{13}C N.m.r. spectra of conjugated pentenynes [a]

	X	XCH$_2$	C(2)	C(3)	C(4)	C(5)
(2*t*-en-4-yn)	Br	30.8	139.8	113.3	80.6	79.8
(2*t*-en-4-yn)	OH	62.4	143.8	109.1	81.7	78.0
(2*c*-en-4-yn)	Br	27.5	139.1	112.1	78.3	85.1
(2*c*-en-4-yn)	OH	60.7	143.6	109.5	79.4	83.4
(2-yn-4-en)	Br	15.0	85.3	84.8	116.4	128.4
(2-yn-4-en)	OH	50.8	87.9	83.8	116.4	127.0

[a] Assignment of the resonances to specific carbon atoms was made by analogy with related compounds (F. D. Gunstone, M. R. Pollard, C. M. Scrimgeour, and H. S. Vedanayagam, *Chem. Phys. Lipids*, 1977, **18**, 115).

Penta-1,4-*diyne* (12).—This was made by the method of Ben-Efraim and Sondheimer in THF solution.[13] Pure diyne was obtained by preparative g.l.c. on a 7 ft glass column packed with 10% ββ'-oxydipropiononitrile operated at 70 °C, *m/e* 64 (M^+), ^{1}H n.m.r. spectrum as in the literature, δ_C 36.0, 85.7, and 96.0 p.p.m.

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