An Electron Spin Resonance Study of Trivinylmethyl and Hepta-2,6-dien-4-ynyl Radicals

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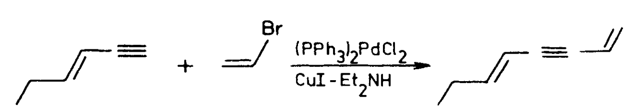
Trivinylmethyl radicals were generated by hydrogen abstraction from trivinylmethane and hepta-2,6-dien-4-ynyl radicals were produced by bromine abstraction from 1-bromohepta-2,6-dien-4-yne. The e.s.r. spectra of the radicals were obtained and the hyperfine splittings compared with computed spin densities. Methane-based stabilisation energies were computed for a variety of delocalised radicals by the semi-empirical UMNDO method. The hydrogen hyperfine splittings of the delocalised radicals were shown to decrease monotonically with increase in the stabilisation energies.

The phenomenon of electron delocalisation in odd conjugated systems can be effectively studied by e.s.r. spectroscopy. Allyl radicals [1,2] and many substituted allyl radicals have been investigated in this way. Recently, interconversion between the planar conformers of pentadienyl radicals was observed by e.s.r. spectroscopy [3-5] and activation parameters for the analogous conformational change in pent-1-en-4-ynyl radicals were obtained.[6] These delocalised radicals are useful models of the more complex species obtained on hydrogen abstraction from unsaturated fatty acids, and comparison with their e.s.r. spectra enabled the main radicals generated from the lipids to be identified.[7,8]

There is also considerable interest in the spin density distribution in delocalised radicals [9-11] and their stabilisation energies [11,12] (resonance energies), which can also be determined by e.s.r. techniques in favourable cases.[6,12] Apart from a few reports on heavily substituted analogues [13,14] nothing is known about acyclic π-radicals in which the unpaired electron is delocalised over seven atoms, although the cyclic analogue cycloheptatrienyl [15] and benzyl radicals [16] have received a good deal of attention. As an extension of our work on delocalised radicals we have generated trivinylmethyl (manxyl) radicals and hepta-2,6-dien-4-ynyl radicals. In this paper we report the e.s.r. spectra and the results of a semi-empirical SCF MO investigation of their structures and stabilisation energies.

$$\underset{(1)}{HC(CH_2CO_2Me)_3} \xrightarrow{Na-EtOH} \underset{(2)}{HC(CH_2CH_2OH)_3} \longrightarrow \underset{(3)}{HC(CH_2CH_2OAc)_3} \xrightarrow{750\,^{\circ}C} \text{other products} + CH_3CO_2H + \underset{(4)}{CH(CH{=}CH_2)_3}$$



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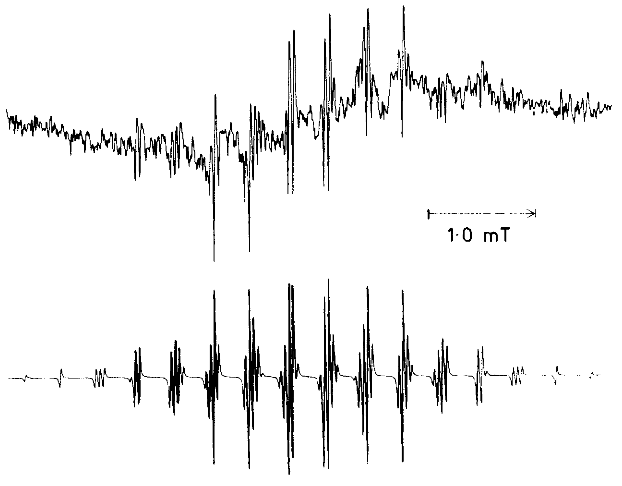


Figure 1. 9.4 GHz e.s.r. spectrum of trivinylmethyl radicals (6a) in cyclopropane at 135 K. Upper spectrum, experimental; lower spectrum, computer simulation

Results and Discussion

Synthesis of Radical Precursors.—3-Vinylpenta-1,4-diene (trivinylmethane) (4) was synthesised by a method outlined in 1951 by Paul and Tchelitcheff.[17] Trimethyl methanetriacetate (1) was reduced to 3-(2-hydroxyethyl)pentane-1,5-diol (2) with sodium in ethanol. The triol (2) was converted to the triacetate (3) which was decomposed by flash vacuum pyrolysis [18] at 750 °C. Reduction of (1) (or the corresponding triacid) by $LiAlH_4$ in ether was not successful despite the earlier report.[17] An alternative synthesis involves condensing ethylene oxide with the anion of pentadiene and converting the resulting 3-vinylpent-4-en-1-ol to the xanthate which is then pyrolysed.[19]

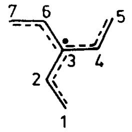
Sonogashira *et al.*[20] and others [21,22] showed that acetylenic hydrogens could be substituted by bromoalkenes in the presence of catalytic amounts of bis(triphenylphosphine)-palladium dichloride and copper(I) iodide in diethylamine. We found that the substitution of *trans*-pent-2-en-4-yn-1-ol by vinyl bromide was catalysed in a similar way provided longer reaction times were employed. The product hepta-2*E*,6-dien-4-yn-1-ol (5) was converted into the trimethylsilyl ether and 1-bromahepta-2*E*,6-dien-4-yne by standard procedures. Attempts to convert (5) into the corresponding heptatriene (for generation of heptatrienyl radicals) by hydrogenation over Lindlar's catalyst were unsuccessful, complex mixtures being obtained.

Generation of Trivinylmethyl and Hepta-2,6-dien-4-ynyl Radicals.—The e.s.r. spectrum shown in Figure 1 was obtained on photolysis of a mixture of trivinylmethane and di-t-butyl peroxide in cyclopropane at 135 K. The spectrum shows hyperfine splittings (h.f.s.) by three different groups of three equivalent hydrogens (see simulation in Figure 1) and can be

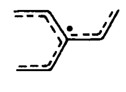
Table 1. E.s.r. parameters of mono-, di-, and tri-vinylmethyl radicals

Radical	Site	H.f.s. (mT)	ρ(π) HMO	ρ(π) INDO	INDO[a] ρ(s)	INDO[a] H.f.s.	ρ(s) CINPRO	ρ(s) UMNDO[b]
$\overset{1}{C}H_2\text{–}\overset{2}{C}H\text{–}\overset{3}{C}H_2$	1 *exo*	1.481	0.5	0.622	−0.0279	−1.51	−0.009 20	−0.0432
	1 *endo*	1.390			−0.0269	−1.45	−0.008 86	−0.0423
	2	0.406	0.0	−0.243	0.0137	0.74	0.004 58	0.0304
$(CH_2\text{–}CH)_2CH$	1 *exo*	1.04	0.333	0.428	−0.0201	−1.08	−0.006 88	−0.0390
	1 *endo*	0.96			−0.0189	−1.02	−0.006 67	−0.0381
	2	0.33	0.00	−0.211	0.0117	0.63	0.004 07	0.0309
	3	1.16	0.333	0.577	−0.0254	−1.37	−0.008 53	−0.0398
$(CH_2\text{–}CH)_3C$	1 *exo*	0.74	0.25	0.257	−0.0173	−0.934	−0.005 73	−0.0367
	1 *endo*	0.70			−0.0165	−0.893	−0.005 48	−0.0355
	2	0.33	0.0	−0.067	0.0108	0.581	0.003 60	0.0311
	3		0.25	0.492				

[a] $\langle S^2\rangle$ = 0.8147(allyl), 0.8520(pentadienyl), 0.8992(trivinylmethyl). [b] $\langle S^2\rangle$ = 0.994(allyl), 1.275(pentadienyl), 1.513(trivinylmethyl)



(6a)



(6b)

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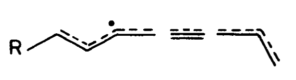


(8)

a; R = H b; R = OSiMe$_3$ c; R = OH

attributed to trivinylmethyl radicals in the planar symmetrical (manxyl) conformation (6a). This was the only observable radical in the temperature range 135—200 K, which shows that (6a) is not converted into the alternative planar conformation (6b) (because this would have a more complex spectrum), nor is (6b) formed by hydrogen abstraction from unsymmetrical conformers of (4). The e.s.r. parameters of (6a) are compared with those of allyl [1,2] and pentadienyl radicals [5] in Table 1.

An e.s.r. spectrum of hepta-2,6-dien-4-ynyl radicals (7a) was obtained by photolysis of a mixture of 1-bromohepta-2*E*,6-dien-4-yne, hexabutylditin, and di-t-butyl peroxide in toluene at 190 K. The e.s.r. spectra of 1-trimethylsiloxyhepta-2*E*,6-dien-4-ynyl (7b) (Figure 2) and 1-hydroxyhepta-2*E*,6-dien-4-ynyl radicals (7c) were observed on hydrogen abstraction from the trimethylsilyl derivative of (5), and (5) itself, by photochemically generated t-butoxyl radicals. The spectrum of (7a) was too weak to examine over a temperature range; the spectrum of (7b) showed minor changes in the h.f.s. with temperature, but only a single radical was visible in the range 160—290 K. The two planar 1-trimethylsiloxypent-2-yn-4-enyl radicals (9) and (10) were found to be spectroscopically indistinguishable; [6] by analogy (7) and (8) should also be indistinguishable by e.s.r. Because the barrier to rotation about the C(5)–C(6) bond in (7) will be low the observed hepta-2,6-dien-4-ynyl radicals are probably a mixture of (7) and (8). Rotation about the C(2)–C(3) bond in (7) and (8) could lead to additional planar conformers, but since the double bond is initially *trans*, and (7) and (8) are the thermodynamically most stable conformers, conversion to other conformers is unlikely.

Comparison with Theory.—The h.f.s. of radicals (6a) and (7) (Tables 1 and 2) were assigned to specific hydrogens by comparison with related radicals.[2,5] In allyl [1,2] and pentadienyl radicals [4,5] hydrogens occupying *exo*-positions on double bonds have larger h.f.s. than hydrogens occupying *endo*-positions. The assignments in Tables 1 and 2 were made on the assumption that a similar relationship would hold for *exo*- and *endo*-hydrogens in (6a) and (7). It would be expected that the h.f.s. of the hydrogens on terminal carbons [C(1) in Table 1] would decrease as the number of atoms in the chain increases and the extent of electron delocalisation increases. For example, according to Hückel theory the coefficients of the molecular orbitals of a straight chain of n atoms are given by [23] $c_{rj} = (2/n + 1)^{\frac{1}{2}}\sin(rj\pi/n + 1)$, where j = number of atom and r = number of orbital. For the terminal atom $j = 1$ and for the semi-occupied orbital (SOMO) $r = (2/n + 1)$ hence $c_1^2 = (2/n + 1)$ and the spin density is predicted to decrease with $(2/n + 1)$. In fact a plot of the $a(H_1)$ values from Table 1 against $(2/n + 1)$ is a reasonably straight line passing through the origin.*

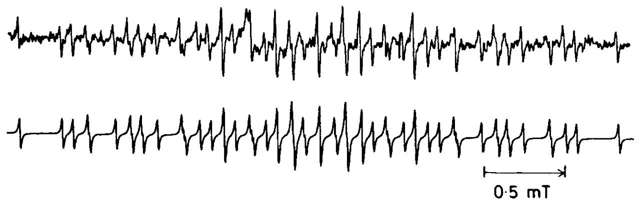
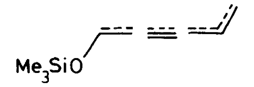


Figure 2. 9.4 GHz e.s.r. spectrum of 1-trimethylsiloxyhepta-2*E*,6-dien-4-ynyl radicals (7b) in neat di-t-butyl peroxide at 245 K. Upper spectrum, experimental; lower spectrum, computer simulation



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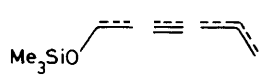

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Calculations were also carried out using the INDO technique [25] employing radical geometries obtained from MNDO calculations. Comparison of the INDO spin densities and h.f.s. (Tables 1 and 2) with experiment shows a good degree of agreement. INDO calculations on allyl and pentadienyl

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* Trivinylmethyl does not contain a straight chain of seven atoms, but the Hückel coefficient at C(1) in the SOMO of (6a) is the same as that of the hepta-2,4,6-trienyl radical.[24]

Table 2. E.s.r. parameters for hepta-2,6-dien-4-ynyl radicals

		H.f.s. (mT)							
Radical	Method	H(1*exo*)	H(1*endo*)	H(2)	H(3)	H(6)	H(7*exo*)	H(7*endo*)	OH
(7c)[a]	Expt.		0.89	0.24	1.24	0.33	0.43	0.42	0.07
(7b)[a]	Expt.		0.98	0.26	1.24	0.33	0.43	0.42	
(7a)[b]	Expt.	1.00	0.91	0.31	1.26	0.32	0.46	0.44	
(7a)	INDO[c]	−1.07	−1.01	0.63	−1.50	0.51	−0.57	−0.54	

[a] At 245 K. [b] At 190 K. [c] $\langle S^2 \rangle = 0.8546$.

radicals with ' standard ' bond lengths and angles predict the h.f.s. of *endo*-hydrogens to be greater than those of *exo*-hydrogens,[1,5] contrary to the experimental findings. The present calculations with optimised geometries show agreement with experiment and confirm the assignments. Spin densities for the hydrogen *s*-orbitals calculated with the UHF version of the MNDO method, *i.e.* UMNDO, are also given in Table 1. These calculated spin densities show a smaller decrease with increasing chain length and overestimate the amount of positive spin density at the hydrogens attached to C(2) even more than the INDO calculations. Calculated values of $\langle S^2 \rangle$ were high for all radicals by both the INDO and UMNDO methods. This indicates that the wave functions contain contaminating contributions from components of higher multiplicity spin states. Spin densities were therefore also calculated for the pure doublet states by complete projection at the INDO level of approximation using the CINPRO program,[27] and are also recorded in Table 1. The projected spin densities show essentially the same correlation with experiment, and the same decrease with increase in chain length, as the INDO results, although their absolute magnitudes are smaller.

The experimental h.f.s. of H(2) in trivinylmethyl radicals (0.33 mT) is equal to that of H(2) in pentadienyl radicals and higher than might have been expected. However, McLachlan pointed out that a high spin density on one atom tends to induce a high negative spin density on the adjacent atom.[28] The spin density on the central atom of (6a), *i.e.* C(3) is higher than would be the case for C(3) of a straight chain radical (see Table 1) and the relatively large h.f.s. of H(2) in (6a) is a consequence of this.

The geometries and enthalpies of formation of (6a and b) were calculated using the UMNDO method. The planar conformer (6a) was predicted to be 12 kJ mol^{-1} more stable than the planar non-symmetrical conformer (6b), and this is consistent with the absence of (6b) in the experimental spectrum. The calculated double bond lengths were 1.38 Å in (6a) and single bond lengths were 1.45 Å; $C(1)\widehat{C}(2)C(3)$ was 130° and $C(2)\widehat{C}(3)C(4)$ was found to be 120°. The methane-based stabilisation energies [5,11] of carbon-centred radicals R· [equation (1)] depend on the extent of delocalisation of the unpaired electron, relief of steric strain, and other factors. In

$$E_s^{MeH} = \Delta H_f(CH_3\cdot) - \Delta H_f(CH_4) - [\Delta H_f(R\cdot) - \Delta H_f(RH)] \quad (1)$$

general E_s^{MeH} would be expected to increase with the extent of electron delocalisation; which can also be measured by means of the e.s.r. hyperfine splittings. Thus an inverse relationship between E_s^{MeH} and the radical h.f.s. would be expected, although it would not be linear but a more complex function. E_s^{MeH} Values are difficult to determine accurately by thermochemical and other methods, and very few are known with good precision. E_s^{MeH} Values calculated by the UMNDO technique for a variety of planar delocalised radicals containing C, H, N, and O and including (6a) and (7) are compared with experimental values in Table 3. The calculated values are the same as the experimental ones, within experimental error, for all except the propynyl radical where the UMNDO result is significantly lower. The computed result for pent-1-en-4-ynyl radicals is also significantly lower than the e.s.r. experimental result; but this was based on the thermochemical value for propynyl radicals,[6] and so does not represent an independent disagreement.

Ideally the E_s^{MeH} values should be compared with ^{13}C h.f.s. of the central atoms in the delocalised radicals, because these would give the most direct measure of electron delocalisation. Rather few ^{13}C h.f.s. are known but for methyl,[30] propynyl,[33] allyl,[34] and benzyl [16] the values are 3.834, 3.39, 2.10, and 2.45

Table 3. Experimental and calculated stabilisation energies of delocalised radicals [a]

	E_s^{MeH}		E_s^{MeH}		
Radical	Thermochem.[b]	E.s.r.	UMNDO	H.f.s. (mT)	No. in Figure 3
$CH_3\cdot$	[0] [c]	[0] [c]	[0] [c]	2.30	1
$CH_3COCH_2\cdot$	28	39 [d]	29	1.97	2
$H_2NCH_2\cdot$	49		54	1.53	3
$HC{\equiv}CCH_2\cdot$	66		44	1.89	4
$H_2C{=}CHCH_2\cdot$	78	66 [e]	68	1.48—1.39	5
$PhCH_2\cdot$	72	~60 [f]	68	1.63	6
$(H_2C{=}CH)_2CH\cdot$	118	>130 [g,h]	131	1.14	7
$(H_2C{=}CH)_3C\cdot$			141	—	8
Pent-1-en-4-ynyl		112 [h]	104	1.38	9
Pent-1-yn-4-enyl			51	1.54	10
Pentadiynyl			83	1.66	11
(7)			96	1.26	12

[a] In kJ mol^{-1}. [b] Based on the bond dissociation energies compiled by McMillen and Golden.[29] [c] Zero by definition. [d] From ref. 30. [e] From ref. 31. [f] From ref. 32. [g] From ref. 5. [h] From ref. 6.

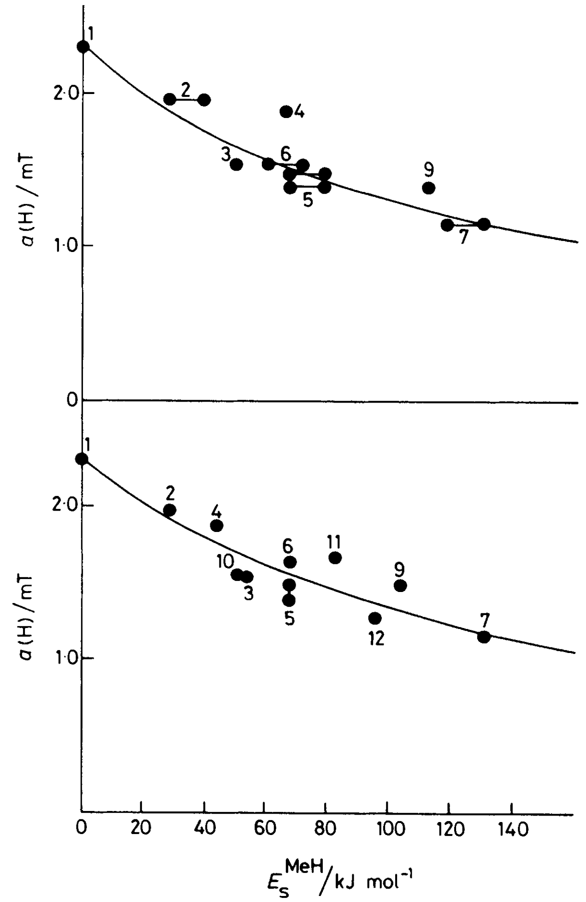

Figure 3. Correlation of methane based stabilisation energies E_s^{MeH} *versus* hydrogen h.f.s. for planar delocalised radicals. Upper panel, experimental E_s^{MeH} values; lower panel, computed E_s^{MeH} values. The key to the numbers is in Table 3

mT respectively, and they show a general decrease with increasing E_s^{MeH}. The hydrogen h.f.s., which are easily measured, are listed in Table 3 and plotted against E_s^{MeH} in Figure 3. The plots of both experimental and calculated E_s^{MeH} are rather scattered due to experimental and computational errors and presumably because steric and other factors are not taken into account. The data can be fitted by a decreasing curve which approaches the E_s^{MeH} axis asymptotically as *a*(H) tends to zero. The plots should be useful for cross-checking measured E_s^{MeH} values. In this connection it should be noted that the correlation with *a*(H), the correlation with the ^{13}C h.f.s., and the UMNDO calculated E_s^{MeH} values all suggest that a reduction in the stabilisation energy of propynyl radicals from 66 to *ca.* 45—50 kJ mol^{-1} is necessary.

Experimental

^1H N.m.r. spectra were recorded on a Bruker WP 80 instrument for $CDCl_3$ 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 AEI MS 902 spectrometer. Preparative g.l.c. was carried out on a Pye 105 instrument with columns packed with Embaphase silicone oil on Chromosorb G. E.s.r. spectra were obtained with a Bruker ER 200D spectrometer. Di-t-butyl peroxide and hexa-n-butylditin were purified as described previously.[6]

3-(2-*Hydroxyethyl*)*pentane*-1,5-*diol* (2).—Methanetriacetic acid [35] was converted to the trimethyl ester with methanol and concentrated H_2SO_4. The triester (6.0 g) in dry ethanol (90 ml) was added to sodium (7.8 g); the solution was refluxed for 30 min after all the sodium had dissolved. Water (3.5 g) was added and the solution was refluxed for a further 3 min until all the solids had dissolved. Concentrated HCl (40 ml) was added to the cooled solution and the mixture was cooled in ice. The precipitated NaCl was filtered off and the filtrate treated with anhydrous potassium carbonate. The alcoholic solution was filtered and the solid extracted several times with boiling ethanol. The ethanol was removed on a rotary evaporator. The crude $CH(CH_2CH_2OH)_3$ was dried by repeatedly adding benzene and removing it on a rotary evaporator, yield 3.0 g, δ_H 1.4—1.8 (6 H, m), 2.0—2.4 (1 H, m), and 3.70 (6 H t, *J* 6 Hz).

Triacetate (3).—The crude triol (2) (1.0 g), acetyl chloride (5.0 g), and pyridine (5.0 g) in $CHCl_3$ (50 ml) were allowed to stand at ambient temperature for 3 days. The solution was then washed with water, 2M-HCl, and water again and dried over Na_2SO_4. The product was purified by column chromatography on silica gel with light petroleum containing 5% ether as eluant, yield 1.1 g. G.l.c. analysis on an SE 30 column at 200 °C indicated *ca.* 95% purity, δ_H 1.70 (6 H, m), 1.7—2.3 (1 H, m), 2.17 (9 H s), and 4.2 (6 H, m), δ_C 167.6 (C=O), 75.5 (t, *J* 24 Hz, CH_2O), 32.4 (t, *J* 24 Hz, $CH_2CH_2CH_2$), 20.9 (q, *J* 27 Hz, CH_3O), and 18.4 p.p.m. (d, *J* 25 Hz, CH).

Flash Vacuum Pyrolysis of Triacetate (3).—Small samples (*ca.* 25 mg) of (3) were subjected to flash vacuum pyrolysis [18] at 650, 700, and 750 °C and 5×10^{-3} Torr pressure. G.l.c. analysis of the pyrolysates indicated that at 650 and 700 °C elimination of acetic acid was incomplete and accordingly a larger sample (0.95 g) was pyrolysed at 750 °C. The pyrolysate contained significant amounts of gaseous material and g.l.c. analysis showed four main volatile components together with minor amounts of long retention time material. The volatile components were separated by preparative g.l.c. on a silicone oil column at 150 °C. The first component was too volatile to trap; the second component (*ca.* 20 mg) was shown to be trivinylmethane, the third component (*ca.* 0.5 g) was acetic acid, and the fourth component was not identified. Trivinylmethane had M^+ 94 (from g.c.–m.s.), δ_H 3.4—3.6 (1 H, m, CH), 5.0—5.3 (6 H, 2 m, $=CH_2$), and 6.2—7.7 (3 H, m, $-CH=$); the assignment was checked by simulation of the spectrum.

Hepta-2E,6-*dien*-4-*yn*-1-*ol* (5).—A mixture of vinyl bromide (15 g), *trans*-pent-2-en-4-yn-1-ol [36] (8.2 g), and $(PPh_3)_2PdCl_2$ (0.07 g) in Et_2NH (100 ml) was stirred under nitrogen and CuI (0.04 g) was added. After 2 h $(PPh_3)_2PdCl_2$ (0.02 g) and CuI (0.01 g) were added and the solution stirred for a further 26 h. The Et_2NH was removed on a rotary evaporator and water was added to the residue to dissolve the crystals. The mixture was extracted with benzene and the benzene layer dried over Na_2SO_4. The benzene was removed on a rotary evaporator and the residual oil was distilled under reduced pressure in a Vigreux flask. Nearly pure (5) was obtained after a short fore-run, b.p. 52—58 °C at 0.25 Torr, yield 5.6 g (52%) (Found M^+, 108.0580. C_7H_8O requires *M*, 108.0575), δ_H 2.4 (1 H, s, OH), 4.15 (2 H, dd, *J* 7, 1.5 Hz), 5.47 (1 H, dd, *J* 10, 4 Hz), 5.7—6.0 (3 H, m), and 6.30 (dt, *J* 4.5, 16 Hz). The ^{13}C n.m.r. data are in Table 4.

The reaction was also carried out with a mixture of *trans*- and *cis*-pent-2-en-4-yn-1-ol [37] to give a mixture of hepta-2*E*,6-dien-4-yn-1-ol and hepta-2*Z*,6-dien-4-yn-1-ol, b.p. 65—70 °C at 1.5 Torr; yield 47%. The ^1H and ^{13}C n.m.r. spectra of the *cis*-compound were obtained from the spectra of the mixture

Table 4. ^{13}C N.m.r. spectra of conjugated 1-X-hepta-2,6-dien-4-ynes [a]

	X	XCH$_2$	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
2*E*,6-dien-4-yne	Br	31.5	138.0	114.4	90.8	87.1	116.9	127.5
2*Z*,6-dien-4-yne	Br	28.2	137.0	113.1	95.9	84.6	116.9	127.4
2*E*,6-dien-4-yne	OH	62.9	141.9	110.4	88.9	88.0	117.2	126.8
2*Z*,6-dien-4-yne	OH	60.9	141.5	110.3	93.5	86.0	117.0	127.0

[a] Assignment of the resonances to specific carbon atoms was made by analogy with related compounds (ref. 6 and F. D. Gunstone, M. R. Pollard, C. M. Scrimgeour, and H. S. Vedanayagam, *Chem. Phys. Lipids*, 1977, **18**, 115).

by substracting the known peaks for the *trans*-isomer; δ_H 1.9 (1 H, s, OH), 4.45 (2 H, dd, J 7, 1.5 Hz), 5.4—5.54 (2 H, dd), and 5.6—6.5 (3 H, m). The ^{13}C n.m.r. data are in Table 4.

1-*Trimethylsiloxyhepta*-2E,6-*dien*-4-*yne*.—Trimethylsilyl chloride (1.09 g) was added dropwise to a solution of hepta-2*E*,6-dien-4-yn-1-ol (5) (1.08 g) and pyridine (0.79 g) in n-pentane (10 ml). After stirring for 1 h the solution was filtered, the pentane was removed on a rotary evaporator, and the residual oil was distilled under reduced pressure in a Vigreux flask to give 1-trimethylsiloxyhepta-2*E*,6-dien-4-yne (0.91 g), b.p. 95—97 °C at 15 Torr, δ_H 0.25 (9 H, s), 4.20 (2 H, dd, J 2, 4.6 Hz), 5.32—5.55 (1 H, dd, J 10, 3.5 Hz), and 6.05—6.45 (4 H, dt, J 14, 4.5 Hz).

1-*Bromohepta*-2E,6-*dien*-4-*yne*.—Hepta-2*E*,6-dien-4-yn-1-ol (2.16 g) and triethylamine (3.0 g) in CH$_2$Cl$_2$ (75 ml) were stirred under nitrogen and cooled in ice while MeSO$_2$Cl (2.52 g) was added over 15 min. The solution was stirred for a further 20 min then water was added, the CH$_2$Cl$_2$ layer was separated, washed with 2M-HCl (100 ml), 5% brine (50 ml), saturated NaHCO$_3$ (100 ml), and then dried over Na$_2$SO$_4$. CH$_2$Cl$_2$ was removed on a rotary evaporator and the crude mesylate was added immediately to a solution of LiBr (3.5 g) in dry acetone (75 ml). The mixture was refluxed for 30 min, the solution was cooled and filtered, and the acetone removed by distillation at atmospheric pressure. Water was added to the residue which was then extracted with ether. The combined ether layers were dried with Na$_2$SO$_4$ and the ether was removed by distillation at atmospheric pressure. The residual oil was distilled under reduced pressure in a Vigreux flask to give 1-bromohepta-2*E*,6-dien-4-yne (1.8 g, 53%), b.p. 85—88 °C at 15 Torr (Found: M^+, 169.9720. $C_7H_7{}^{79}Br$ requires M, 169.9732), δ_H 4.0 (2 H, d, J 7 Hz), 5.50 (1 H, dd, J 4, 10 Hz), 5.65—6.05 (3 H, m), and 6.1—6.5 (1 H, dt, J 8, 16 Hz). The ^{13}C n.m.r. data are in Table 4.

The mixture of *cis*- and *trans*-hepta-2,6-dien-4-yn-1-ols was converted to the bromides by a similar procedure, yield 45%, b.p. 53—60 °C at 15 Torr, *m/e* 170, 172 (M^+), δ_H 4.20 (2 H,d J 7 Hz), 5.60 (1 H, dd, J 4, 10 Hz), and 5.7—6.5 (4 H, m). The ^{13}C n.m.r. data are in Table 4.

Hydrogenation of (5) *over Lindlar's Catalyst*.—The heptadienynol (5) (2.4 g), Lindlar's catalyst [38] (0.3 g), and quinoline (0.3 g) were stirred in ethyl acetate (20 ml) under hydrogen. Uptake of hydrogen proceeded smoothly to well beyond one mol equiv. The solution was filtered, washed with 2M-HCl (2 × 50 ml), dried over Na$_2$SO$_4$, and the ethyl acetate removed on a rotary evaporator. The residual oil was distilled under reduced pressure giving 0.75 g of material boiling at 75—83 °C and 15 Torr. The ^{1}H n.m.r. spectrum showed this to be a complex mixture of products. Several hydrogenations were carried out in which the hydrogen uptake was stopped before one mol equiv. had been absorbed. In each case, however, the product proved to be a complex mixture. Direct hydrogenation of 1-bromohepta-2*E*,6-dien-4-yne over Lindlar's catalyst was also attempted, but no hydrogen uptake could be achieved.

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