Electron Delocalisation and Stabilisation in Heptatrienyl and Polyenyl Radicals

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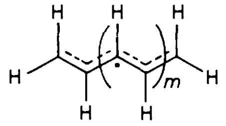
Heptatrienyl radicals were generated by hydrogen abstraction from hepta-1,3,6-triene with t-butoxyl radicals and observed by e.s.r. spectroscopy. The hyperfine splittings of heptatrienyl and other polyenyl radicals indicate that spin density is not uniformly distributed along the chain but more concentrated around the central region of the structure. Semi-empirical SCF MO calculations agree with this result and also show that most radical character is associated with the central region. The stabilisation energies (SE) of polyenyl radicals increase with chain length and are related to the hydrogen hyperfine splittings as in equation (i) where $a(H^1)$ is the average of the *anti*- and *syn*-hydrogen hyperfine splittings (G) of

$$SE^{ESR}/kJ\ mol^{-1} = 375 \pm 4 - (272 \pm 10)\log_{10}[a(H^1)/G] \qquad (i)$$

the terminal methylene groups.

Electron delocalisation in different molecular frameworks leads to a number of chemically important phenomena including resonance stabilisation and aromaticity. When the molecule contains an odd number of π-orbitals, each with one electron, the resulting species is a free radical. The distribution of unpaired spin and, in favourable cases, the stabilisation energies of these species can be effectively studied by e.s.r. spectroscopy. The archetype species for π-electron delocalisation in a linear sense are the polyenyl radicals (**1**). However, only the first two members of the series, allyl (**1**; m = 0) and pentadienyl radicals (**1**; m = 1) had previously been observed. Allyl[1,2] and substituted allyl radicals have been extensively investigated by e.s.r. spectroscopy. The barrier to rotation about the C(1)–C(2) partial double bond in allyl radicals was determined by steady-state kinetic e.s.r. measurements,[3] and this led to a value for the allyl stabilisation energy. In pentadienyl radicals the e.s.r. hyperfine splittings (h.f.s.) are less than in allyl radicals and the barrier to rotation about the C(2)–C(3) bond is less, as would be expected from the greater extent of delocalisation.[4-6]

Apart from the intrinsic theoretical interest[7-9] of polyenyl radical e.s.r. spectra, they have the very practical usefulness of serving as models for more complex species obtained from natural products. A comparison of the e.s.r. spectra of the archetype polyenyl radicals with those obtained on hydrogen abstraction from unsaturated fatty acids enabled the main radicals generated from the lipids to be identified.[10,11] The archetype 7-π-electron polyenyl radical, *i.e.* heptatrienyl (**1**; m = 2) proved to be very elusive, although some related 7-π-electron radicals, *i.e.* trivinylmethyl (**2**) and hepta-2,6-dien-4-ynyl (**3**), were recently observed.[12] In this paper we report the generation of heptatrienyl radicals and a study of their structure by e.s.r. spectroscopy, aided by semi-empirical SCF MO calculations.



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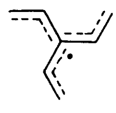

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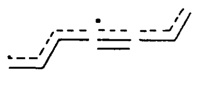

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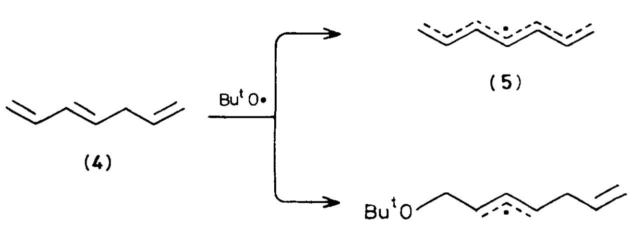


(4)

(5)

(6)

Results and Discussion

Generation of Heptatrienyl Radicals.—The ideal precursor for radicals (**1**) would be 1-bromohepta-2,4,6-triene. Bromine abstraction from this, with silicon- or tin-centred radicals, would give the desired species. However, attempts to prepare this bromide *via* hydrogenation of hepta-2*E*,6-dien-4-yn-1-ol over Lindlar's catalyst gave complex mixtures of products.[12] Attempts to prepare the bromide *via* suitable Wittig syntheses were also unsuccessful. t-Butoxyl radicals abstract hydrogen from penta-1,4-diene to give pentadienyl radicals, but they preferentially add to conjugated double bonds,[13] and only adduct radicals were observed with penta-1,3-diene.[6] It would be expected therefore that t-butoxyl radicals would preferentially add to hepta-1,3,5-triene, rather than abstract hydrogen to give heptatrienyl radicals. In hepta-1,3,6-triene (**4**) there is a choice between abstraction of the bisallylic hydrogens at C(5) to give heptatrienyl radicals (**5**) and addition to the conjugated double bonds to give the adduct radical (**6**). It seemed likely that hydrogen abstraction would be the favoured route and (**4**) was accordingly synthesised by the reaction of vinylmagnesium bromide with *trans*-1-bromopenta-2,4-diene in THF.[14] The reaction gave a low yield of (**4**) together with two dimers of the pentadiene moiety, (**7**) and (**8**), and minor amounts of toluene. Sufficient (**4**) was isolated from the mixture by preparative g.l.c. for the e.s.r. study.

The e.s.r. spectrum shown in Figure 1 was obtained on photolysis of a mixture of (**4**) and di-t-butyl peroxide in CCl_2F_2 at 145 K; similar spectra were obtained in cyclopropane and neat di-t-butyl peroxide as solvents. The spectrum shows h.f.s. by four different groups of two equivalent hydrogens and by a unique hydrogen (see simulation in Figure 1) and can be

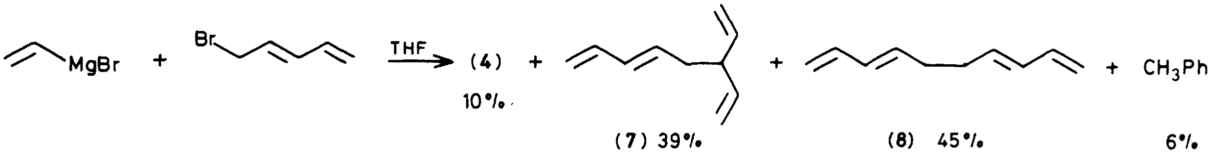


Table 1. E.s.r. parameters of polyenyl radicals

Radical	Site	T/K	H.f.s. (G)	INDO h.f.s. (MINDO/3 geom) (G)	INDO h.f.s. (UMNDO geom) (G)
$CH_2{-}\dot{C}H{-}CH_2$	1,3 *anti*	143	14.81	−15.1	−14.9
	1,3 *syn*		13.90	−14.5	−14.7
	2		4.06	7.4	7.3
$CH_2{-}CH{-}\dot{C}H{-}CH{-}CH_2$	1,5 *anti*	233	10.4	−10.8	−11.1
	1,5 *syn*		9.6	−10.2	−11.2
	2,4		3.3	6.3	6.6
	3		11.6	−13.7	−13.1
$\overset{1}{C}H_2{-}\overset{2}{C}H{-}\overset{3}{C}H{-}\overset{4}{\dot{C}}H{-}\overset{5}{C}H{-}\overset{6}{C}H{-}\overset{7}{C}H_2$	1,7 *anti*	145	7.8	−8.4	−8.4
	1,7 *syn*		7.3	−7.8	−8.3
	2,6		2.7[a]	5.2	5.3
	3,5		9.5	−11.6	−11.7
	4		3.3[a]	7.3	7.3
$CH_2{-}CH{-}\dot{C}{-}({-}CH{-}CH_2)_2$	1,5,7 *anti*	135	7.4		−9.3
	1,5,7 *syn*		7.0		−8.9
	2,4,6		3.3		5.8

[a] $\partial a/\partial T = 1.7$ mG K^{-1}.

attributed to heptatrienyl radicals in the planar all-*trans* conformation (**5**). The spectrum was unchanged in the temperature range 150—240 K, apart from increases in the two smallest h.f.s. No signals attributable to the adduct radicals (**6**) were detectable and abstraction of the bisallylic hydrogens is the major reaction pathway. In the temperature range 150—120 K, in CCl_2F_2 solvent, the spectrum showed a marked weakening in intensity, but no new signals could be distinguished.

The e.s.r. parameters of heptatrienyl radicals are compared with those of other polyenyl radicals in Table 1. The doublet h.f.s. of 3.3 G can be immediately assigned to the unique H(4) and the triplet splitting of 2.7 G to H(2) and H(6). Both these h.f.s. showed small positive temperature coefficients of about the same magnitude as that found for the analogous hydrogens of allyl and pentadienyl radicals. This is good evidence that these h.f.s. are positive.[4,6] The ratio of the 7.8 and 7.3 G triplet splittings (*i.e.* 1.07) is essentially identical to the ratio of the h.f.s. of the *anti*- and *syn*-hydrogens in both allyl and pentadienyl radicals. This presumably reflects a similar structural relationship[5] and these h.f.s. can be assigned to the *anti*- and *syn*-hydrogens H(1) and H(7) in (**5**). It follows that the triplet h.f.s. of 9.5 G corresponds to the equivalent pair H(3) and H(5).

There are five low-energy planar conformations of heptatrienyl radicals, (**5**) and (**9**)—(**12**) [excluding structures with sterically crowded *U* (*i.e. Z,Z*) arrangements], which might be produced by hydrogen abstraction from the various conformers of (**4**). For pentadienyl radicals two planar conformers were distinguished on hydrogen abstraction from penta-1,4-diene at low temperatures, but isomerisation to the *W*-conformer was observed above 180 K. By analogy it would be expected that the heptatrienyl radical conformers would also isomerise to the lowest energy all-*trans*-conformer (**5**) by rotation about the partial double bonds in the appropriate (lower) temperature range. In fact only the all-*trans* conformer could be detected in the accessible temperature range, but the weakening of the signals intensity below 150 K could well have been caused by the overlapping of signals from some or all five species, it being impossible to distinguish individual lines. At temperatures above *ca.* 150 K isomerisation to (**5**) prevails and this is therefore the only detectable conformer. Under typical e.s.r. conditions the rate constant for a unimolecular isomerisation is *ca.* 10^3 s^{-1} when the concentrations of the unrearranged and rearranged species are equal.[15] The temperature at which this situation is reached cannot be accurately determined, but appears to be at or below 150 K. Taking a 'normal' pre-exponential factor of 10^{13} s^{-1},[16] the activation energy for bond rotation in (**5**) is estimated to be $\leqslant 35$ kJ mol^{-1}.

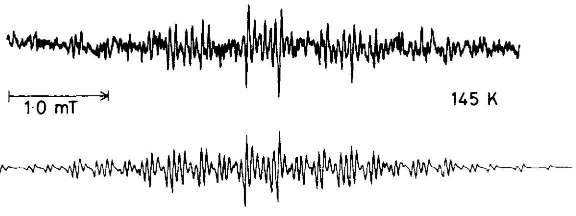
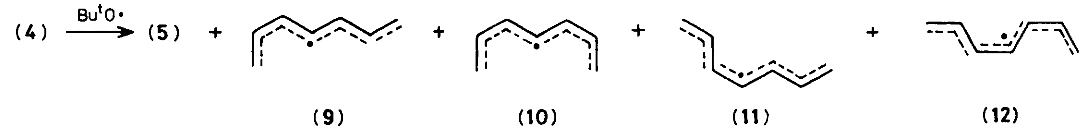


Figure 1. 9.4 GHz e.s.r. spectrum of heptatrienyl radicals (**5**) in CCl_2F_2 at 145 K. Upper trace, experimental; lower trace, computer simulation

Hyperfine Splittings in Acyclic Polyenyl Radicals.—We intuitively expect that the h.f.s. of hydrogens in polyenyl radicals should decrease in magnitude as the number of carbons in the chain, *n*, increases and the extent of delocalisation increases. The results in Table 1 show that this is indeed the case and the h.f.s. of H(1), H(2), and H(3) all decrease with increase in *n*. For convenience we focus attention on the h.f.s. of the terminal methylene groups [H(1)]. Figure 2 shows a plot of the



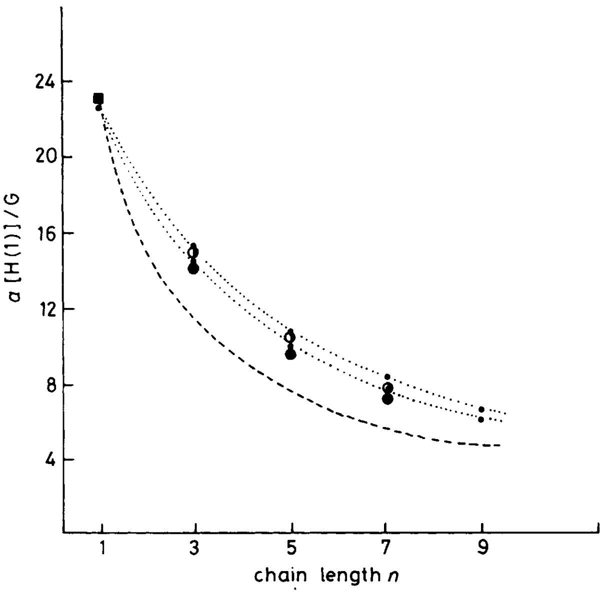


Figure 2. Correlation of e.s.r. hyperfine splittings a[H(1)] with chain length for polyenyl radicals. Filled square, methyl radicals; half filled circles, experimental data for *syn*-hydrogens of terminal methylene groups {a[H(1)*syn*]}; filled circles, analogous data for *anti*-hydrogens. Small circles and dotted lines, INDO calculations, upper line *syn*-hydrogens, lower line *anti*-hydrogens. Dashed line, HMO predictions

H(1)(*anti*) and H(1)(*syn*) h.f.s. against chain length n. The experimental data can be satisfactorily represented by the logarithmic functions (1) and (2). The correlation coefficient is

$$a[\mathrm{H}(1)anti]/\mathrm{G} = 23.1 \pm 0.24 - (7.83 \pm 0.16)\ln(n) \quad (1)$$
$$a[\mathrm{H}(1)syn]/\mathrm{G} = 22.9 \pm 0.23 - (8.15 \pm 0.16)\ln(n) \quad (2)$$

0.9996 in both cases. According to the well known McConnell relation, $\bar{a}(\mathrm{H}) = Q_{\mathrm{CH}}^{\mathrm{H}\rho^{\pi}}$, where $Q_{\mathrm{CH}}^{\mathrm{H}}$ has a value of *ca.* 23 G. Thus the experimental data for acyclic polyenyl radicals suggest equation (3), where b is a constant of value *ca.* 1/3. This

$$\rho_1^{\pi}(\text{polyenyl}) = 1 - b\ln(n) \quad (3)$$

empirically derived expression serves as a useful summary of the data; a theoretical interpretation would obviously be desirable.

According to HMO theory[12] $\rho_1^{\pi} = 2/(n + 1)$, but the plot of this function (Figure 2) using $Q_{\mathrm{CH}}^{\mathrm{H}}$ 23 G to convert ρ_1^{π} into h.f.s., shows too steep a decrease for the initial points. The h.f.s. of polyenyl radicals calculated by the INDO method[17] depend on the geometries taken for the individual radicals. Using geometries obtained from MINDO/3 and UMNDO calculations (*vide infra*) the INDO h.f.s. recorded in Table 1 were obtained. The calculated h.f.s. reproduce the experimental data quite well: for a given radical the order of the h.f.s. is always correctly predicted. The INDO calculations overestimate, however, the amount of negative spin density on C(2), C(4), *etc.*, and this leads to values of a(H^2], *etc.*, which are too large. The INDO values of a(H^1), derived from the MINDO/3 geometries, are plotted in Figure 2. There is quite reasonable agreement and the INDO results come quite close to reproducing the right trend. The difference between the experimental and INDO curves is significantly greater than the errors of measurement of the h.f.s. and the INDO calculations underestimate the decrease in a(H^1) with increase in n. This is connected with the overestimate of the negative spin density on C(2), *etc.*, and is a consequence of the fact that electron correlation is not sufficiently well handled by the semi-empirical INDO method.

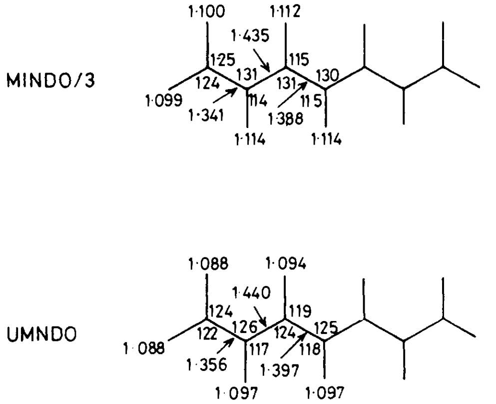


Figure 3. Optimum geometries for heptatrienyl radicals (5) calculated by semi-empirical MO theory. Upper structure, MINDO/3 prediction: lower structure, UMDO prediction. Bond lengths in Angstroms and bond angles in degrees .

The optimum structures of heptatrienyl radicals calculated by the MINDO/3[18,19] and UMNDO[20] methods are shown in Figure 3. The results indicate C–C bonds intermediate in length between single and double, which alternate along the chain, with the terminal bonds shortest. The MINDO/3 calculations suggest shorter C–C bond lengths and wider C–C–C bond angles than the UMNDO calculations. The deviation of the C–C–C and H–C–C bond angles from 120° probably occurs to relieve steric compression. There is some indication of alternation in the C–H bond lengths, the terminal C–H bonds being shortest in each case. Comparison of these structures with those for the other polyenyl radicals indicates that most radical character becomes concentrated in the centre of the molecules; the outer wings becoming more alkene-like with increasing chain length. Likewise, the spin density is concentrated in the centre of the radicals and this becomes more pronounced with increasing chain length; the INDO-calculated spin densities (Table 1) reveal this clearly.

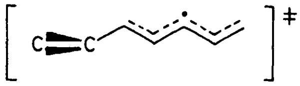
The experimental h.f.s. support these predictions. In pentadienyl radicals the ratio a[H(3)]/a[H(1)] 1.12 and the magnitude of the inner hydrogen h.f.s. relative to the outer hydrogen h.f.s. is even greater in heptatrienyl radicals {a[H(3)]/a[H(1)] 1.22}. Similarly, in heptatrienyl radicals a[H(4)] significantly exceeds a[H(2)]. Thus the experimental evidence also reveals a concentration of unpaired electron density in the centre of the polyenyl radicals. The electron density is not evenly distributed along the chain as simple π-MO theories suggest. In the absence of steric effects polyenyl radicals will have greatest reactivity associated with carbon atoms near the centre of the structure.

Stabilisation Energies of Polyenyl Radicals.—In the transition state (13) for the isomerisation of the all-*trans* conformer (5) to

Table 2. Barriers to rotation and stabilisation energies of polyenyl and related radicals[a]

Radical	E_i E.s.r.	SE^{ESR} [b]	SE^{MH} [c] Thermochem	SE^{CH_3H} [d] Thermochem	SE^{CH_3H} [d] MINDO/3	SE^{CH_3H} [d] UMNDO
Methyl		0	0	0	0	0
Allyl	66[e]	61	48[f]	77[f]	63	67
Pentadienyl	46[g]	102	77[h]	120[h]	75	121
Heptatrienyl	$\leqslant 35$	$\leqslant 133$			109	146
Pent-2-en-4-ynyl	49[i]	96			67	105
Benzyl	54[j]	50	42[k]	71[k]		67
Acetylmethyl	39[l]	35	0—21[m]	29—50[m]		
1-Cyanoallyl	41[n]	73				

[a] In kJ mol^{-1}. [b] The SE^{ESR} values given here differ from those in ref. 12 because (i) SE^{ESR} values rather than thermochemical estimates have been used and (ii) because 4 kJ mol^{-1} has been allowed for V_2 in equation (4). [c] Model based stabilisation energies, *i.e.* relative to n-propyl or isopropyl radicals as appropriate. [d] Methane-based stabilisation energies, *i.e.* relative to methyl radicals. [e] From ref 3. [f] From refs. 23—26. [g] From ref. 6. [h] From refs. 27—30. [i] From ref. 31. [j] From ref. 32. [k] From ref. 27. [l] From refs. 33, 22. [m] From refs. 34—36. [n] From ref. 37.



(**13**)

the conformation (**9**) the unpaired electron is confined to a pentadienyl moiety. The barrier to rotation (E_i) is thus given by equation (4), where $SE^{ESR}(R\cdot)$ is the stabilisation energy of

$$E_i = V_2 + SE^{ESR}(R\cdot) - SE^{ESR}(S\cdot) \qquad (4)$$

heptatrienyl radicals, $SE^{ESR}(S\cdot)$ is the stabilisation energy of the pentadienyl radicals, and V_2 is the barrier to rotation about the *single* bond C(2)–C(3) in the absence of delocalisation. Two-fold barriers, such as V_2, are normally very small.[21,22] Thus the suggestion of *ca.* 4 kJ mol^{-1} for V_2 seems the most reasonable.[3] The stabilisation energy of pentadienyl radicals is known and hence an upper limit for SE^{ESR}(heptatrienyl) can be derived from the upper limit to the rotational barrier E_i, *i.e.* SE^{ESR}(heptatrienyl) $\leqslant$ 33 kJ mol^{-1}. The barriers to rotation and stabilisation energies of polyenyl and related radicals are collected in Table 2 and compared with thermochemical estimates and values calculated by the semi-empirical SCF MO methods.

E.s.r.-derived SE values should contain negligible contributions from inductive–hyperconjugative effects, whereas methane-based stabilisation energies SE^{CH_3H} contain the full contribution from these effects and stabilisation energies based on model compounds overcompensate for them.[38] The SE^{ESR} values should therefore fall between the two thermochemically derived values. Table 2 shows that this is indeed the case for all the radicals, with the possible exception of acetylmethyl. There are some doubts about the thermochemistry of this radical[34—36,38] which have been underlined by the recent demonstration of appreciable barriers to rotation in α-(alkoxycarbonyl)alkyl radicals such as $\cdot CH_2COOR$.[39] Bearing in mind that the SE^{ESR} values are expected to be *ca.* 15 kJ mol^{-1} less than the SE^{CH_3H} values it can be seen that the UMNDO calculations are quite successful at predicting stabilisation energies; MINDO/3 calculations generally underestimate.

In general the SE values are expected to increase with the extent of electron delocalisation, which can also be measured by means of the e.s.r. h.f.s. [equations (1) and (2)]. Thus an inverse relationship between SE and the h.f.s. of the terminal hydrogens of each radical $a(H^1)$ would be expected.[12] In fact a linear correlation of SE^{ESR} values with log $a(H^1)$ can be obtained, equation (5), for which a correlation coefficient of 0.997 was

$$SE^{ESR}/\mathrm{kJ\ mol^{-1}} = 375 \pm 4 - (272 \pm 10)\log_{10}[a(H^1)/G] \qquad (5)$$

found. In deriving this equation the average of the *syn*- and *anti*-h.f.s. was used and the acetylmethyl datum was excluded. Equation (5) reproduces all the SE^{ESR} values to within the experimental error, except for acetylmethyl. The $a(H^1)$ values are relatively easily determined by e.s.r. spectroscopy so that equation (5) can be used for checking and estimating stabilisation energies for a variety of radicals whose rotational barriers cannot be determined. An independent means of determining the inductive–hyperconjugative stabilisation is needed in order to make possible direct comparison of the SE^{ESR} values with thermochemical data.

Experimental

^1H N.m.r. spectra were recorded with 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 instrument. Preparative g.l.c. was carried out on a Pye 105 chromatograph with a 15 ft glass column packed with 12% ββ′-oxydipropiononitrile on Chromosorb W. E.s.r. spectra were obtained with a Bruker ER 200D spectrometer. Samples were prepared in 4-mm diameter Spectrosil quartz tubes, in cyclopropane, dichlorodifluoromethane, and neat di-t-butyl peroxide, degassed and photolysed in the cavity of the spectrometer with light from a 500 W Wotan high-pressure Hg lamp.

Reaction of Vinylmagnesium Bromide with trans-1-*Bromopenta*-2,4-*diene*.—*trans*-1-Bromopenta-2,4-diene was prepared by bromination[40] of the corresponding alcohol[41] with PBr_3. Vinylmagnesium bromide (45 ml of 1M solution in THF) was added drop by drop to a refluxing solution of *trans*-1-bromopenta-2,4-diene (4.5 g in 10 ml THF).[14] The solution was refluxed for 5 h, cooled, and poured into ice-cold ammonium chloride solution. The mixture was extracted with ether; the ether layers were dried and the solvent removed by distillation. The resulting liquid was examined by g.l.c. and g.l.c.–m.s. which showed the presence of four major components in addition to solvent. These were separated by preparative g.l.c. and identified as follows: peak 1 (9.8%), hepta-1,3,6-triene (**4**); δ_H 2.86 (t, J 6 Hz, 2 H), 4.95—5.30 (m, 4 H), and 5.50—6.62 (m, 4 H); m/z 94 (M^+), 91, 79, 77, 54, 53, 41, and 39; peak 2, toluene (6.1%); δ_H 2.37 (s, 3 H) and 7.25 (s, 5 H); M^+, 92; peak 3 (39%), 3-vinylocta-1,5,7-triene (**7**); δ_H 2.25 (t, 2 H, J 7 Hz), 2.83 (quintet, 1 H, J 7 Hz), and 4.85—6.70 (m, 11 H); δ_C 37.7, 47.6, 114.7 (× 2), 115.1, 132.6, 137.2, and 140.5 p.p.m; m/z 134 (M^+), 119, 106, 93, 92, 91, 79, 77. 67, 65, 54, 41, and 39; peak 4 (45.1%), deca-1,3,7,9-tetraene (**8**); δ_H 2.20 (distorted triplet, 4 H) and 4.90—6.70 (m, 10 H); δ_C 32.2, 115.0, 131.5, 134.2, and 137.2 p.p.m; *m/z* 134 (M^+) followed by same ions as for peak 3.

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