Dimers of Delocalised Radicals: Pentamethylcyclopentadienyl and Pentadienyl

Peter N. Culshaw,[a] John C. Walton,*[a] Lise Hughes[b] and Keith U. Ingold[b]
[a] *University of St. Andrews, Department of Chemistry, St. Andrews, Fife, UK, KY16 9ST*
[b] *National Research Council of Canada, Steacie Institute for Molecular Sciences, Ottawa, Canada, K1A 0R6*

The thermal dissociation of bis(pentamethylcyclopentadienyl) to pentamethylcyclopentadienyl radicals has been studied by EPR spectroscopy in the temperature range 365–393 K. The enthalpy of dissociation of the dimer is found to be 18.8 kcal mol^{-1} and combination of this result with empirical and semi-empirical estimates of the enthalpies of formation of the dimer and of pentamethylcyclopentadiene, leads to $\Delta H^\circ_f(\mathrm{Me_5C_5^\bullet}) = 10.7$ kcal mol^{-1}, $DH^\circ(\mathrm{Me_5C_5{-}H}) = 70.6$ kcal mol^{-1} and $E_s^{\mathrm{MeH}}(\mathrm{Me_5C_5^\bullet}) = 34.2$ kcal mol^{-1} (where E_s^{MeH} is the methane-based stabilisation energy). Steric strain is shown to be a major factor leading to weakening of the inter-ring bond of the dimer. The pentaethyl and pentamethoxycarbonyl analogues have been investigated, but neither is suitable for quantitative measurements.

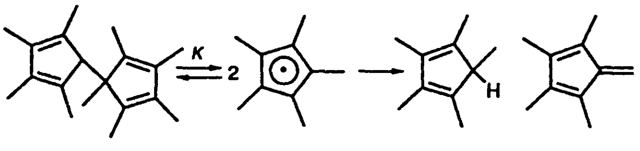
Thermal decomposition of *trans,trans*-deca-1,3,7,9-tetraene and *trans,trans*-3,8-dimethyldeca-1,3,7,9-tetraene gives rise to pentadienyl and 3-methylpentadienyl radicals respectively, each of which isomerises to form a mixture of *trans-* and *cis*-radicals which then couple in both the 'end to end' and 'end to centre' modes to give mixtures of tetraenes. Hydrogen abstraction from 1,2-diphenylhydrazine is not competitive with pentadienyl radical combination in the temperature range 450–490 K. The EPR spectra of pentadienyl and 3-methylpentadienyl radicals have been observed in this temperature range.

The thermal cleavage of a dimer has frequently been employed as a means of generating a specific free radical, and hence studying its structure and modes of reaction. Rüchardt and Beckhaus have successfully used this method, particularly with sterically congested alkanes,[1–3] to probe the effects of strain and electron delocalisation on carbon–carbon bond properties. Occasionally the dimer of a carbon-centred radical is found to be in equilibrium with measurable amounts of the radical at readily accessible temperatures. In this case the radical is usually strongly thermodynamically stabilised by steric and/or electronic effects. That triphenylmethyl[4] and related[5] radicals are in equilibrium with their dimers has been known for a long time. The thermodynamics of only a few other such equilibria have been studied. This includes Russian work on 2-arylindanedione-1,3-diyl radicals[6] and recent detailed studies by Koch and co-workers on a series of substituted 2-oxopiperazin-3-yl radicals.[7] In a pioneering study Vincow *et al.* used EPR spectroscopy to monitor the concentration of the cycloheptatrienyl radical, generated by thermal cleavage of liquid bis(cyclohepta-2,4,6-trien-1-yl), and hence deduced the enthalpy of dissociation, the 'resonance energy', and the enthalpy of formation of the cycloheptatrienyl radical.[8]

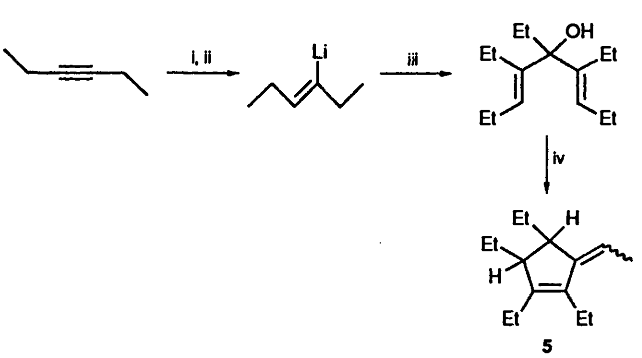
It appeared to us that this method might be useful for determining thermodynamic parameters for other strongly resonance stabilised radicals. Bis(cyclopenta-2,4-dienyl) isomerises too readily into alternative dimers for it to be a suitable substrate. However, Davies and Lusztyk have shown that bis(pentamethylcyclopenta-2,4-dienyl) (**2**) dissociates cleanly to pentamethylcyclopentadienyl radicals (**1**) on thermolysis or photolysis.[9] We report in this paper our study of the thermodynamics of this equilibrium. In addition, since pentadienyl and 3-methylpentadienyl radicals have been shown to be strongly resonance stabilised,[10] we also prepared dimers of pentadienyl and several methyl-substituted pentadienyls and studied their thermal cleavage by EPR spectroscopy and product analysis.

Results and Discussion

Pentasubstituted Cyclopentadienyl Radicals.—Bis(pentamethylcyclopentadienyl) (**2**) was made by treatment of 1,2,3,4,5-pentamethylcyclopenta-1,3-diene with butyllithium and copper(I) chloride.[11] We attempted to prepare the pentaethyl analogue of **2** by a similar method, *i.e.*, *via* 1,2,3,4,5-pentaethylcyclopenta-1,3-diene, synthesised in the same way as pentamethylcyclopenta-1,3-diene.[12] Unfortunately the final acid-catalysed cyclisation step gave a mixture of (*E*)- and (*Z*)-isomers of **5** instead, Scheme 1. Bis(pentamethoxycarbonylcyclopentadienyl) (**7**) was prepared by treating 1,1,2,3,4,5,6,7-octamethoxycarbonylcyclohepta-3,5-diene with potassium acetate to obtain potassium pentamethoxycarbonylcyclopentadiene (**6**) which was converted into **7** by reaction with ceric ammonium nitrate in methanol/water[13,14] (Scheme 2).

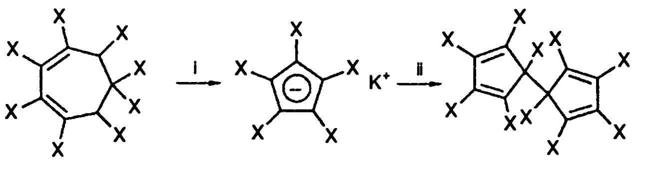


2 **1** **3** **4**



Scheme 1 *Reagents and conditions:* i, HBr; ii, Li/Et$_2$O; iii, EtCO$_2$Me; iv, 4-MeC$_6$H$_4$SO$_3$H, conc. H$_2$SO$_4$

The pentamethylcyclopentadienyl radical was generated in



X = CO_2Me **6** **7**

Scheme 2 *Reagents and conditions:* i, $MeCO_2K/H_2O$; ii, $(NH_4)_2Ce(NO_2)_6/H_2O/MeOH$

Table 1 Radical concentrations and equilibrium constants for pentamethylcyclopentadienyl in hexadecane solution

T/K	[**2**]/10^{-3} mol dm^{-3}	[**1**$^\cdot$]/10^{-8} mol dm^{-3}	$K/10^{-14}$ mol dm^{-3}
365	49.0	3.51	2.51
371	49.0	4.13	3.49
376	49.0	4.96	5.01
382	49.0	5.99	7.33
382	53.6	6.61	8.12
388	49.0	7.36	11.1
388	52.7	15.1	43.5
393	52.7	18.6	65.6

Table 2 Enthalpies of formation of pentamethylcyclopentadiene (**3**) and bis(pentamethylcyclopentadienyl) (**2**) calculated by empirical and semiempirical methods[a]

Molecule	GC	MM2[b]	MNDO	AM1
3	−6.9	−8.7	−3.4	1.4
2	3.4	1.5	48.4	33.5

[a] Values in kcal mol^{-1}. [b] Includes π-conjugation energy.

the cavity of an EPR spectrometer by heating a degassed solution of **2** in hexadecane at temperatures in the range 365–393 K. The resulting spectrum, which consisted of 16 lines [a(15 H) = 0.64 mT], was identical to that described in the literature.[9] The equilibrium constants for the dimer $\rightleftharpoons$ 2 radical system ($K = [1^\cdot]^2/[2]$) were determined at a series of temperatures by measuring the concentration of radical **1**, in solutions of known concentration of **2**, using the EPR method.[15] At each temperature the radical concentration remained virtually constant for many minutes at temperatures < 375 K. Above this temperature the radical concentration was observed to decrease gradually on a timescale of minutes. It has been reported[9] that a minor proportion of radicals **1** disproportionate irreversibly to give pentamethylcyclopentadiene (**3**) and tetramethylfulvene (**4**). We attribute the loss of signal intensity to the occurrence of this process which eventually depletes the stock of dimer. Evidence supporting this conclusion was the development of a bright yellow colour in the reaction mixtures after prolonged heating at high temperatures, a colour which can be attributed to tetramethylfulvene.[9] To compensate for the depletion of dimer at higher temperatures (382–393 K) the radical concentration was measured at known times; extrapolation to zero time yielded the initial (*i.e.* unperturbed) radical concentration. Dimer and radical concentrations, and the corresponding equilibrium constant, are given in Table 1 for each temperature.

The equilibrium constant is related to the enthalpy of dissociation (ΔH°) by the integrated van't Hoff eqn. (1) where

$$\ln K = -\Delta H^\circ/RT + \text{const.} \qquad (1)$$

ΔH° is assumed to be independent of temperature over the 30 K temperature interval of these experiments. The bottom two entries in Table 1, which are less reliable because they were derived from high temperature extrapolations, do not fit well with the rest. Neglecting these two points a good straight line ($r^2 = 0.994$) was obtained from which $\Delta H^\circ = 18.8 \pm 0.7$ kcal mol^{-1} (1 cal = 4.18 J) was derived. This enthalpy of dissociation is related to the enthalpies of formation of radical **1** and its dimer as shown in eqn. (2):

$$\Delta H^\circ = 2\Delta H^\circ_f(\mathbf{1}) - \Delta H^\circ_f(\mathbf{2}) \qquad (2)$$

It follows that the enthalpy of formation of radical **1** could be calculated if the enthalpy of formation of the dimer **2** were known. Although this latter quantity has not been measured experimentally, it can be estimated by empirical and semiempirical methods, the most reliable of which are Benson's Group Contributions (GC) method,[16] and the Allinger Molecular Mechanics approach. The group contribution for $[C\text{-}(C_d)_2(C)_2]$ was not available, but this was extrapolated from the known values for $[C\text{-}(C)_4]$ and $[C\text{-}(C_d)(C)_3]$, *i.e.* $\Delta H^\circ_f[C\text{-}(C_d)_2(C)_2] = 3.86$ kcal mol^{-1}. Simple addition of the group contributions, including ring strain and gauche terms gives 3.4 kcal mol^{-1} as the enthalpy of formation of the dimer. The structure and enthalpy of formation of **2** were also assessed by carrying out molecular mechanics calculations (MM2)[17,18] and semiempirical SCF MO calculations[19] (MNDO[20] and AM1[21]). The computed geometries indicated that serious strain was associated with the inter-ring bond since this was found to be significantly longer than a normal parafinic C–C bond (1.53 Å), the computed bond lengths being 1.56, 1.61 and 1.55 Å by the three methods, respectively. The bond angles of the atoms at the ends of this bond also differed significantly from tetrahedral. The total strain energy, as calculated by the MM2 method, was 33.4 kcal mol^{-1}. This high strain energy obviously contributes to weakening of the inter-ring bond and is one reason why radical **1** forms so easily from **2**. The enthalpies of **2** computed by the various methods are compared in Table 2. The empirical GC and MM2 results are expected to be close to the true result for a hydrocarbon such as **2**. The satisfactory agreement between these two methods lends confidence to the reliability of the estimates. We have arbitrarily taken the average of the GC and MM2 enthalpies as our recommended value, *i.e.* $\Delta H^\circ_f(\mathbf{2}) = 2.5$ kcal mol^{-1}. The ΔH°_f values derived from the SCF MO computations are potentially less reliable because experimental data from model compounds are incorporated in a far less direct way. The MNDO and AM1 methods would appear to overestimate $\Delta H^\circ_f(\mathbf{2})$ by large amounts (Table 2), but these calculations do support the conclusion that dimer **2** is a highly strained molecule.

The enthalpy of formation of radical **1** derived from eqn. (2) by use of the average $\Delta H^\circ_f(\mathbf{2})$ value is given in Table 3. The $\Delta H^\circ_f(\mathbf{1})$ values calculated by the semiempirical AM1 and MNDO methods again exceed the 'experimental' result by large margins. The bond dissociation energy of the bisallylic C–H bond in **3**, *i.e.* $DH^\circ(\mathbf{1}\text{–H})$, is related to $\Delta H^\circ_f(\mathbf{1})$ as indicated in eqn. (3):

$$DH^\circ(\mathbf{1}\text{–H}) = \Delta H^\circ_f(\mathbf{1}) + \Delta H^\circ_f(H^\cdot) - \Delta H^\circ_f(\mathbf{3}) \qquad (3)$$

Enthalpies of formation of **3** estimated by the GC, MM2 and SCF MO methods are listed in Table 2. In this case the spread of values is comparatively small, probably because **3** does not contain much strain other than its (known) ring strain. Thus the total strain energy of **3** calculated by the MM2 method was 8.3 kcal mol^{-1}, nearly all of which can be accounted for as ring strain. Using the average of the GC and MM2 enthalpies of formation of **3** [$\Delta H^\circ_f(\mathbf{3}) = -7.8$ kcal mol^{-1}] in eqn. (3) we obtain $DH^\circ(\mathbf{1}\text{–H}) = 70.6$ kcal mol^{-1}, which is significantly

Table 3 Thermodynamic parameters for cyclopentadienyl and pentamethylcyclopentadienyl radicals[a]

Radical	ΔH°_f Exptl.	AM1	MNDO	DH° (R–H)	E_s^{MeH}
Pentamethylcyclopentadienyl (**1**)	10.7	26.0	16.0	70.6 [77.1[b]]	34.2
Cyclopentadienyl	60.9[c]			[81.2,[b] 81.1[c]]	23.6

[a] Values in kcal mol^{-1}; methane-based stabilisation energies, E_s^{MeH}, based on DH°(Me–H) = 104.8 kcal mol^{-1} (ref. 24). [b] From ref. 22. [c] From ref. 25, 26.

Table 4 Product development during thermolysis of deca-1,3,7,9-tetraene (**10**) at 475 K in hexadecane solution[a]

Thermolysis time/h	**10**[b]	**12**	**13**
0.0	100	0	0
0.5	72	18	10
1.0	68	21	11
1.5	55	30	15
2.25	55	29	16
3.25	56	26	18
4.75	59	24	16
5.5	62	23	15

[a] Yields given as mol % of the total tetraenes. [b] Contained 9% of **11**.

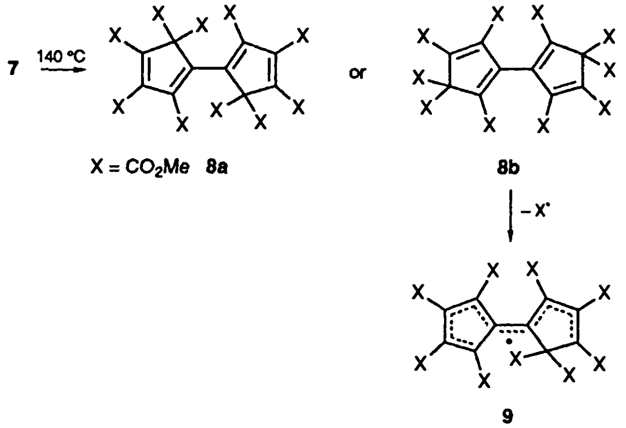
lower than a value obtained recently from pK(**3**) and the oxidation potential of the pentamethylcyclopentadienyl anion[22] (Table 3). The electrochemical method is highly indirect, the results are influenced by solvent effects and by any lack of reversibility in the redox processes. The sizes of corrections for these factors are difficult to judge and may not have been applied.[22] We believe that our result is to be preferred.

The stabilisation energies of delocalised radicals have been defined in various ways.[10,23] One useful method compares the stabilisation of other radicals with that of the methyl radical; *i.e.* a methane-based stabilisation energy E_s^{MeH}, which is defined in eqn. (4):

$$E_s^{\mathrm{MeH}}(\mathrm{R}^\bullet) = DH^\circ(\mathrm{Me{-}H}) - DH^\circ(\mathrm{R{-}H}) \qquad (4)$$

This simple definition of stabilisation energy makes no pretence of distinguishing between resonance stabilisation due to electron delocalisation and stabilisation due to other factors such as relief of steric strain in the parent hydrocarbon, hyperconjugation and inductive effects; it just quantifies the total stabilisation due to all these factors. The methane-based stabilisation energy of **1**, derived by use of the DH°(Me–H) value recently reported by Gutman and co-workers,[24] is compared in Table 3 with data for the cyclopentadienyl radical.[25,26] This shows that the bisallylic C–H bond of the pentamethyl compound is 10.6 kcal mol^{-1} weaker, and hence E_s^{MeH}(**1**) is 10.6 kcal mol^{-1} greater than for the cyclopentadienyl radical. This increase in stabilisation due to methyl substitution is in line with expectation. Thus, although a single alkyl substituent has only a minor effect on the stabilisation energies of open chain allyl and pentadienyl radicals,[10,27] five methyl substituents would be expected to increase significantly electron delocalisation *via* hyperconjugative and/or inductive effects. We conclude that the very low bond dissociation energy of dimer **2** is due both to stabilisation of the radical **1** and to steric strain in the dimer. The pentaisopropylcyclopentadienyl radical was isolated recently by Sitzmann as a crystalline solid which was characterised by X-ray structure analysis and other spectroscopic techniques.[28] The absence of dimer formation for this species is probably a consequence of the even greater steric strain which would be present in the dimer.

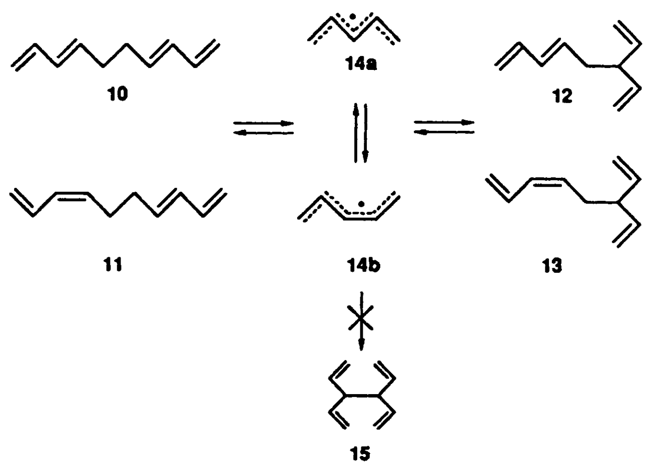
Thermolysis of the decamethoxycarbonyl-dimer **7** in the EPR cavity at 385 K gave rise to a spectrum of the corresponding pentamethoxycarbonylcyclopentadienyl radical [a(15 H) = 0.066 mT] which was similar to one that had been described in the literature.[29] However, at this temperature, this spectrum was overlapped by a broad, strong signal from another radical. This second spectrum was not due to an impurity because repeated recrystallisation of **7** (which showed no impurity peaks in its NMR spectra) had no effect on the EPR signal intensities. Analysis of the product after thermolysis indicated that dimer **7** had isomerised to give **8a** or **8b** (Scheme 3). Loss of a methoxycarbonyl radical from **8** on heating would give a highly delocalised radical such as **9**, or an isomer. We attribute the broad spectrum to radical **9** or a mixture of isomers of **9**. Because this broad spectrum badly masked the signals from the pentamethoxycarbonylcyclopentadienyl radical we were not able to make accurate measurements of the radical concentration. This system therefore proved to be unsuitable for thermodynamic measurements.



Scheme 3

Pentadienyl and Methyl-substituted Pentadienyl Radicals.— We also examined the thermal cleavage of several pentadienyl dimers. (E),(E)-Deca-1,3,7,9-tetraene (**10**) was made by the copper(I) chloride-catalysed coupling of pentadienylmagnesium bromide with 5-bromopenta-1,3-diene. On heating **10** (containing a minor amount of **11**) in hexadecane or *tert*-butylbenzene solution in the absence of oxygen it slowly isomerised to a mixture of four tetraenes, **10**, **11**, **12** and **13**. The proportions of the three main dimers as a function of thermolysis time at 475 K are given in Table 4. None of the middle-to-middle dimer, **15**, was detected. A likely mechanism for the isomerisation is outlined in Scheme 4. Homolysis of the central C(5)–C(6) bond of **10** should occur comparatively readily because this will generate the delocalised pentadienyl radical **14a** which, at the thermolysis temperature, can isomerise to **14b** by internal rotation. Coupling of pentadienyl radicals can take place at the terminal or central atoms and the products can all redissociate to pentadienyl radicals, which should lead eventually to an equilibrium mixture of the four dimers. Although pure samples of **12** and **13** were not obtained, thermolysis of a mixture of **12** and **13** under the same conditions led to the same four dimers in about the same proportions.

The tetraene **10** is potentially capable of undergoing a thermal electrocyclic Cope rearrangement to give **15**. However, uncatalysed Cope rearrangements of unsubstituted dienes analogous to **10** require higher temperatures than we employed.[30] Also an electrocyclic rearrangement cannot explain the formation of the unsymmetrical tetraenes **11**–**13**. Thus, it is



Scheme 4

Table 5 Product development during thermolysis of **16** and **17** at 473 K in hexadecane solution[a]

Thermolysis time/h	**16**	**17**	**18**	**19**
0.0	85.3	13.0	1.6	0.1
2.25	59.4	37.7	1.6	0.6
4.75	42.9	54.1	1.6	1.4

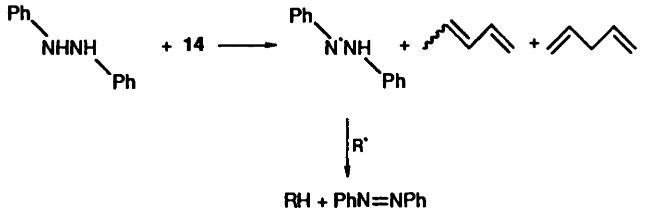
[a] Yields given as mol % of the total tetraenes.

unlikely that the Cope process makes a significant contribution to the overall reaction.

Table 4 shows that the proportions of both **12** and **13** increased for about the first 2 h of thermolysis but subsequently declined. The total amount of dimer present in solution also declined during the thermolysis reaching *ca.* 20% of the early (0.5 h) concentration in the final (5.5 h) mixture. During the reaction a white solid, which was probably a polymer (see Experimental section) separated from the solution, and the GC–MS analysis indicated additional minor products. It appears, therefore, that the system proceeds towards equilibrium, as depicted in Scheme 4, but that the tetraenes take part in additional reactions, particularly polymerisation, which deplete their concentrations. The decline in the [**12**]/[**10**] and [**13**]/[**10**] ratios in the later stages of the thermolysis (Table 4) is probably due to some selectivity for **12** and **13** in these side reactions.

Thermolysis of **10**, and the **12** + **13** mixture, was also examined in hexadecane solution by EPR spectroscopy. At 480 K and above, weak signals showing the central lines of the spectrum[31] of radical **14** were visible. This provides further evidence that the mechanism of Scheme 4 is correct. Unfortunately, the complex signal of radical **14** was too weak for quantitative measurements. A weak signal of this type, at the limits of EPR detection, indicates that the radical concentration must have been $\leqslant 10^{-7}$ mol dm^{-3} at 480 K. Thus we can roughly estimate that the equilibrium constant was $\leqslant 3 \times 10^{-15}$ mol dm^{-3} at 480 K. The 'equilibrium constant' in this context would of course be a weighted mean of the equilibria shown in Scheme 4.

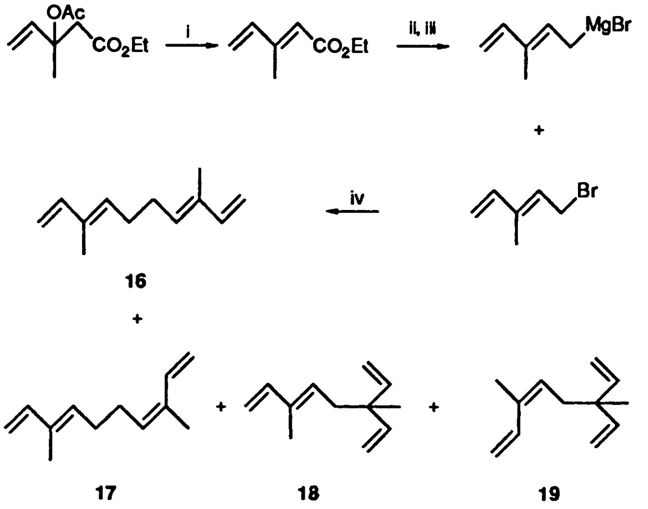
Experiments were also carried out in an attempt to trap radical **14** and hence indirectly determine its concentration by product analysis. Most of the usual radical traps were unsuitable either because they are unstable at 480 K, or because they would react with the unsaturated bonds of the tetraenes. We therefore chose (*E*)-1,2-diphenylhydrazine to react with the radicals formed from **10** in a heated hexadecane solution. We hoped that the pentadienyl radicals would abstract hydrogen from this trap to give a mixture of (*E*)- and (*Z*)-penta-2,4-dienes and penta-1,5-diene more rapidly than they would couple, and that the resonance stabilised 1,2-diphenylhydrazyl radical would simply be converted into azobenzene (Scheme 5).



Scheme 5

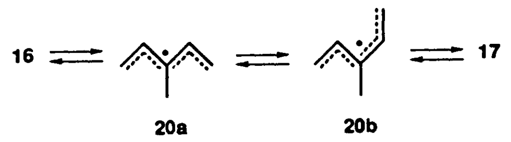
Thermolyses were carried out at 450, 470 and 490 K and the products were monitored periodically by GC–MS and UV–VIS spectroscopy over a period of 4.5 h. No pentadienes or azobenzene could be detected. Instead, tetraene **10** isomerised to give the same mixture of tetraenes previously encountered. Thus, hydrogen abstraction from diphenylhydrazine by **14** was not fast enough to compete with pentadienyl radical coupling.

We investigated two additional 'dimers' which we expected would thermolyse to give delocalised pentadienyl radicals. First, we reasoned that 3,8-dimethyldeca-1,3,7,9-tetraene (**16**) should undergo homolysis of the central C(5)–C(6) bond to give 3-methylpentadienyl radicals. This delocalised radical should be inhibited from coupling at the central carbon atom for steric reasons and hence a simpler equilibrium should result. Tetraene **16** was made by the copper(I) chloride-catalysed coupling of 3-methylpenta-2,4-dienylmagnesium bromide with 5-bromo-3-methylpenta-1,3-diene. Preparative gas chromatography of the mixture of tetraenes obtained in this way gave **16** (85%) as a mixture with the 3,4-(*E*)-isomer **17** (13%) and traces of the unsymmetrical 'end-to-centre' dimers **18** and **19** (Scheme 6).



Scheme 6 *Reagents and conditions:* i, FVP/570 °C; ii, $LiAlH_4$; iii, PBr_3/C_5H_5N then Mg/Et_2O; iv, CuCl

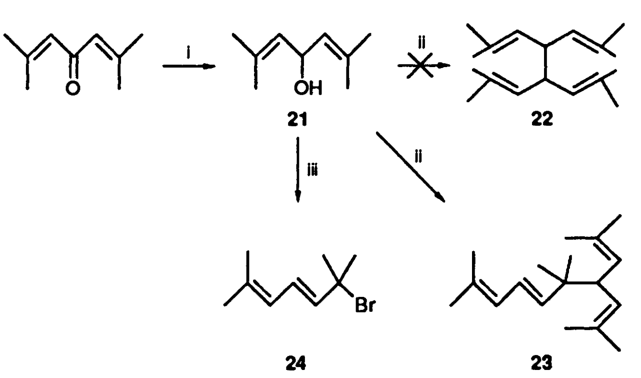
Upon thermolysis of this mixture at 473 K in hexadecane none of the 'centre-to-centre' dimer was formed and the amounts of both 'end-to-centre' dimers, **18** and **19**, were negligible (Table 5). Thus, the methyl substituent was indeed sufficiently bulky to block all but a trivial amount of central coupling. The main thermal process was an isomerisation which converted the (*E*)-isomer **16** into the (*Z*)-isomer **17**, eventually giving a mixture containing a slight preponderance of **17**. It seems probable that this takes place by internal rotation about the C(2)–C(3) partial double bond in the intermediate 3-methylpentadienyl radical **20** (Scheme 7) since this type of bond rotation has been observed previously on heating pentadienyl radicals.[31,32]



Scheme 7

Thermolysis of **16** in hexadecane was examined by EPR spectroscopy, but the corresponding 3-methylpentadienyl radicals were not detectable even at 500 K. However, when a sample of tetraene **18** was heated at $T \geqslant 470$ K a very weak spectrum (central few lines only) of the 3-methylpentadienyl radical[32] was observed. Once again the quality of the spectrum was much too poor for quantitative measurements. Thus, although this methyl-substituted system was chemically simpler than the parent pentadienyl system, it was not suitable for thermodynamic measurements. However, we can say that the dimer/radical equilibrium constant must be similar in magnitude to that for the unsubstituted system.

Second, we planned to divert the coupling process in favour of centre-to-centre coupling by using four methyl substituents at the ends of the pentadienyl unit. The synthesis of tetraene **22** was therefore attempted as outlined in Scheme 8. Unfortunately, treatment of alcohol **21** with McMurray's reagent afforded a mixture of viscous products the main component being the 'end-to-centre' dimer **23**. The possibility of preparing **22** or **23** by the CuCl-catalysed coupling of the corresponding bromide and Grignard was also examined. However, bromination of alcohol **21** gave rearranged bromide **24** which was too unstable for further chemical manipulation.



Scheme 8 *Reagents and conditions:* i, $LiAlH_4$; ii, $TiCl_3/LiAlH_4$; iii, HBr

Conclusions

Thermal cleavage reactions of dimers of cyclopentadienyl and pentadienyl radicals take place at comparatively low temperatures to produce the expected delocalised radicals. The systems of double bonds in the dimers and radicals generally makes them susceptible to a variety of reactions in addition to the desired radical–radical coupling. Thus, only in exceptional cases, such as that of the sterically well shielded and highly symmetrical pentamethylcyclopentadienyl radical, are these thermolyses suitable for thermodynamic measurements. The pentamethyl dimer **2** undergoes thermal cleavage at temperatures which are nearly 100 K lower than those required to cleave the pentadienyl dimer **10**. This striking difference in behaviour is the result of both the steric strain in **2** and the greater stabilisation of the product radicals which appreciably weaken the inter-ring bond. The present results are compared with analogous thermodynamic data for other equilibria between a dimer and two radicals in solution (Table 6). We conclude that the extent of steric strain in a substrate should always be assessed, alongside the stabilisation energies of the intermediate radicals, when mechanistic possibilities are being evaluated.

Experimental

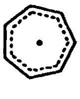
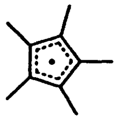
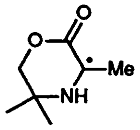
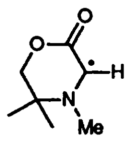
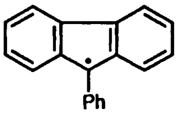
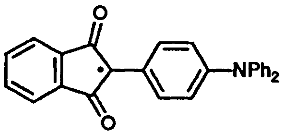
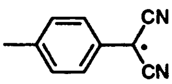
^1H NMR spectra were obtained with Bruker WP 80 (80 MHz) and Bruker AM 300 (300 MHz) spectrometers. The latter instrument operating at 75 MHz was used for ^{13}C NMR spectra. Samples were dissolved in $CDCl_3$; Me_4Si was used as internal standard; J values are in Hz. EPR spectra were recorded at 9.3 GHz with a Bruker ER 200D instrument employing 100 kHz modulation. Samples were prepared in *tert*-butylbenzene or hexadecane solution, degassed by bubbling nitrogen for 10 min and photolysed in the spectrometer cavity with light from a 500 W super pressure mercury arc. GC–MS analyses were carried out with a Finnigan Incos 50 quadrupole mass spectrometer coupled to a Hewlett-Packard HP 5890 capillary gas chromatograph fitted with a column coated with methylsilicone stationary phase. Preparative GLC was carried out with a Pye-Unicam 105 chromatograph.

EPR Measurement of Radical Concentrations.[15]—Solutions of known concentration of **2** were heated in the EPR cavity and a single line, the second most intense on the low field side of the spectrum, was recorded at each temperature. In the higher temperature experiments this line was recorded at a series of times after insertion of the sample into the pre-heated cavity. The initial signal intensity was then obtained by extrapolation to zero time. Radical concentrations were determined by double integration of this line and comparison with the spectrum of a known concentration of DPPH. Both sample and DPPH spectra were normalised with respect to the constant signal from a ruby disc situated off centre in the cavity.

1,1′,2,2′,3,3′,4,4′,5,5′-*Decamethylbis(cyclopentadienyl)*[11] (**2**).—To a solution of 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (1.0 g, 7.34 mmol) in dry diethyl ether (28 cm^3) was added, under N_2, methyllithium (6.2 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 9.3 mmol). The solution was refluxed overnight to afford a white suspension of lithium pentamethylcyclopentadienide. This was allowed to cool and freshly prepared copper(I) chloride (0.65 g, 6.57 mmol) and dry ether (28 cm^3) were added. The mixture was stirred under nitrogen for 5 h. After this time the solution had turned black and a thin copper mirror was observed on the walls of the flask. The solution was evaporated to give a bright green solid. Water and diethyl ether were added to the solid and the ether was then separated. The aqueous layer was further extracted with ether (3 x 20 cm^3), the combined ether layers were dried (Na_2SO_4) and evaporated to give a yellow oil which eventually crystallised. The product was purified by crystallisation from methanol, m.p. 48–49 °C, δ_H 1.13 (6 H, s), 1.66–1.72 (24 H, m) (Found: C, 88.5; H, 11.3. Calc. for $C_{20}H_{30}$: C, 88.82; H, 11.18%).

Reaction of 3-*Bromohex*-3-*ene with Methyl Propanoate.*—To a well stirred solution of small pieces of lithium wire (0.49 g, 71 mmol) in dry diethyl ether (70 cm^3) under argon was added a small portion of 3-bromohex-3-ene (5.7 g, 35 mmol). After the reaction began, the remainder of the bromide was added at a sufficient rate to maintain gentle reflux. It was then stirred for 1 h after which time unchanged lithium was removed. A solution of methyl propanoate (1.57 g, 18 mmol) in dry ether (2 cm^3) was added dropwise. An exothermic reaction occurred and the solution became milky. The solution was then poured onto saturated ammonium chloride solution (45 cm^3). The aqueous layer was removed and was adjusted to pH 9 with dilute HCl before extracting with ether. The combined ether layers were

Table 6 Comparison of thermodynamic parameters of dimers (R_2) and delocalised radicals ($R^{\bullet}$)[a]

Radical	$\Delta H^{\circ}(R_2)$	$\Delta H^{\circ}_{f}(R^{\bullet})$	$DH^{\circ}(R{-}H)$	$E_s^{MeH}(R^{\bullet})$	Refs.
	35	64.8	72.2	32.6[b]	8
	—	60.9	81.2	23.6	22, 25, 26
	18.8	10.7	70.6	34.2	This work
	35.9[c] (21.5)[d]		75.3	29.5	7, 38
	(26.4)[e]		77.5	27.3	7, 38
	25.4				5
	17.8				6
	9.1				6, 39

[a] All in kcal mol^{-1}. [b] From eqns. (3) and (4) using data of ref. 8. [c] In benzene; much lower values were obtained in more polar solvents. [d] In absolute ethanol. [e] In 95% ethanol.

dried (Na_2SO_4) and evaporated to *ca.* 5 cm^3. The concentrate was added to a solution of toluene-*p*-sulfonic acid in dry ether (7 cm^3). No reaction was observed so a few drops of conc. H_2SO_4 were added. The reaction mixture became warm and some water separated. After stirring for 5 min the solution was poured onto saturated sodium hydrogen carbonate solution (45 cm^3) and the excess of acid was neutralised by addition of solid sodium carbonate. The ether layer was removed and the aqueous layer was extracted with ether. The combined ether layers were dried (Na_2SO_4), evaporated and distilled on a Kugelrohr at 153 °C/14 Torr. δ_H 0.79–1.15 (12 H, m), 1.72 (3 H, d, CH_3), 1.93–2.34 (10 H, m), 5.70 (1 H, q, CH); *m/z* (%) 206 (M^+, 30), 191 (28), 177 (100), 163 (9), 149 (27), 135 (15), 121 (31), 107 (20), 93 (25), 77 (11). These spectra were consistent with the substituted fulvene structures **5**.

1,1′,2,2′,3,3′,4,4′,5,5′-*Decamethoxycarbonylbis(cyclopentadienyl)* (**7**).[14]—To a stirred solution of potassium pentamethoxycarbonylcyclopentadienide[13] (0.5 g, 1.27 mmol) in 50% methanol/water (3 cm^3) was added a solution of ceric ammonium nitrate (0.7 g, 1.27 mmol) in 50% methanol/water (3.75 cm^3). The solution was stirred for 30 min, filtered, washed with ice-cold 50% methanol/water and pumped dry to give a white solid which was recrystallised from methanol (× 3) to give **7** (0.4 g, 44%); m.p. 170 °C (lit.,[14] 175–176 °C); δ_H 3.69 (6 H, s), 3.81 (12 H, s), 3.83 (12 H, s); δ_C 53.33, 54.42, 67.88, 139.55, 141.21, 161.67, 164.24.

Thermal Rearrangement of **7**.—Dimer **7** (*ca.* 100 mg) in *tert*-butylbenzene was heated at 120–140 °C until a red-brown colour developed. The solvent was removed on a rotary evaporator and by pumping with a rotary oil pump. The residue was taken up in $CDCl_3$; δ_H 3.71 (12 H, s), 3.81 (6 H, s), 3.83 (6 H, s), 3.87 (6 H, s); δ_C 53.95, 54.20, 54.45, 55.55 (all CH_3), 133.74 (C), 142.54 (C), 158.98 (CO), 161.22 (CO); *m/z* (%) 710 (M^+, 6), 667 (74), 652 (12), 636 (14), 546 (16), 532 (35), 499 (12), 458 (11), 426 (12), 414 (12), 396 (15), 355 (10), 293 (20). These spectra were consistent with structure **8a** or **8b**.

Copper(I) *Chloride-catalysed Reaction of* 5-*Bromopenta*-1,3-*diene with Penta*-2,4-*dienylmagnesium Bromide*.—5-Bromopenta-1,3-diene (3.0 g, 20 mmol) in dry THF (6 cm^3) was slowly added to magnesium (0.55, 23 mmol) in THF (3 cm^3) containing a crystal of iodine and a drop of 1,2-dibromoethane under nitrogen. The Grignard reagent was refluxed for *ca.* 0.5 h and then copper(I) chloride (0.27 g) was added and the solution was refluxed for a further 10 min. 5-Bromopenta-1,3-diene (3 g, 20 mmol) in THF (6 cm^3) was then added slowly and the mixture was refluxed for 20 h. The product mixture was cooled, poured onto ice/water containing NH$_4$Cl which was then extracted with diethyl ether. The ether layer was washed with saturated NaCl solution, dried (Na$_2$SO$_4$) and evaporated to give a mixture of tetraenes (5.4 g, 99%). This mixture was separated by preparative gas chromatography using a 1 m column packed with Carbowax 20M maintained at 58 °C. The first major peak collected was shown by GC–MS and NMR to be a mixture of (*E*)-3-vinylocta-1,5,7-triene (**12**) (32%); δ_H 2.24 (2 H, t, *J* 6.8), 2.81 (1 H, pentet, *J* 5.8), 4.9–5.2 (6 H, m), 5.6–5.8 (3 H, m), 6.07 (1 H, dd, *J* 10.3, 15.2), 6.30 (1 H, dt, *J* 10.3, 16.6); δ_C 37.7, 47.6, 114.7 (2 unresolved), 115.1, 132.6, 137.2, 140.5; *m*/*z* (%), 134 (M$^+$, 10), 119 (24), 116 (9), 115 (8), 106 (14), 105 (46), 92 (32), 91 (100), 79 (47), 67 (100), and (*Z*)-3-vinylocta-1,5,7-triene (**13**) (1%); δ_H 2.34 (2 H, dt, *J* 7.3, 1.4), 2.81 (1 H, m), 5.20 (1 H, m), 4.9–5.3 (5 H, m), 5.44 (1 H, dd, *J* 7.8, 18.5), 5.6–5.8 (2 H, m), 6.07 (1 H, m), 6.62 (1 H, dt, *J* 10.8, 16.6); *m*/*z* (%) 134 (M$^+$, 1), 119 (5), 93 (7), 92 (8), 91 (8), 79 (6), 77 (6), 67 (100). The second peak was mainly (*E*),(*E*)-deca-1,3,7,9-tetraene (**10**); δ_H 2.18–2.20 (4 H, m), 4.97 (2 H, d, *J* 9.8), 5.10 (2 H, d, *J* 17.1), 5.66–5.73 (2 H, m), 6.07 (2 H, dd, *J* 10.2, 15.1), 6.31 (2 H, dt, *J* 9.8, 17.1); δ_C 32.2, 115.0, 131.5, 134.2, 137.2; *m*/*z* (%) 134 (M$^+$, 1), 119 (6), 92 (13), 91 (6), 79 (7), 77 (6), 67 (100), 65 (18). The NMR spectra showed that this peak contained *ca.* 9% of another dimer. The spectra of this minor component were partly obscured by the signals from **10**, but we identify it as (*E*),(*Z*)-deca-1,3,7,9-tetraene (**11**); δ_H 2.3 (4 H, m), 5.0 (2 H, m), 5.19 (2 H, d, *J* 16.6), 5.44 (2 H, dd, *J* 8.0, 18.6), 5.6–5.7 (2 H, m), 6.62 (2 H, dd, *J* 11.2, 16.6); δ_C 27.4, 32.4, 115.0, 117.1, 129.7, 131.4, 132.2, 134.2, 137.2, 139.1.

Thermolysis of **10**.—The tetraene **10** (0.02 g, 0.15 mmol) in hexadecane (0.5 cm^3), with pentadecane (0.01 g) as internal standard, was degassed by bubbling nitrogen for 10 min and then heated at 200 °C in a tube sealed with a septum. Small samples were withdrawn at timed intervals and analysed by GC–MS. The tetraenes **12** and **13** were identified from their retention characteristics and mass spectra (see above). The relative proportions of the tetraenes are given in Table 4. At the end of the heating period (5.5 h) a white solid had separated. This was filtered, washed with pentane and dried. The EI mass spectrum showed a series of ions every 14 mass units extending to at least C$_{17}$H$_{35}^+$. The solid was partly soluble in CDCl$_3$, but the ^{1}H NMR spectrum showed only broad ill-defined absorption in the aliphatic region. We conclude that the solid is a saturated polymer.

Thermal Reaction of **10** *with* (E)-1,2-*Diphenylhydrazine*.—The tetraene **10** (100 mm^3), (*E*)-1,2-diphenylhydrazine (0.2 g) and octane (50 mm^3) as internal standard, in hexadecane (4 cm^3) were heated at 180 °C for 4.5 h. Samples were withdrawn at timed intervals and analysed by GC–MS and by UV–VIS spectroscopy. No pentadienes or azobenzene were detected, but a mixture of the tetraenes **10**, **12** and **13** developed as the thermolysis proceeded. Thermolyses were also carried out at 200 and 220 °C with similar results.

Ethyl 3-*Methylpenta*-2,4-*dienoate*.—Ethyl 3-methyl-3-acetoxypent-4-enoate[33] (12.0 g portions) was subjected to flash vacuum pyrolysis at 570 °C/10^{-2} Torr. Products from several runs were collected in cooled traps (liq. N$_2$), combined, dissolved in dichloromethane, washed with sat. NaHCO$_3$ solution to remove acetic acid, dried (Na$_2$SO$_4$) and distilled. The ^{1}H NMR spectra of the *E* and *Z* isomers overlapped extensively but were in good agreement with the literature;[34] δ_H 1.26 (t, CH$_3$ *E*/*Z* overlap), 2.00 (3 H, s, CH$_3$ *Z*), 2.28 (3 H, s, CH$_3$ *E*), 4.18 (q, *E*/*Z* overlap), 5.02–5.80 (m, CH$_2$ *E*/*Z* overlap), 6.35–6.48 (m, CH *E*/*Z* overlap), 7.83 (2 H, dd, CH *E*, *J* 19, 16); δ_C(*E*-isomer) 14.23, 20.00, 59.64, 117.98, 119.29, 140.06, 151.79, 166.67; δ_C(*Z*-isomer) 12.86, 24.76, 60.71, 119.82, 120.18, 133.93, 150.64, 165.89; *m*/*z* (%) 140 (M$^+$, 51), 112 (70), 111 (68), 97 (38), 95 (100), 67 (75), 55 (25).

3-*Methylpenta*-2,4-*dien*-1-*ol*.—A solution of ethyl 3-methylpenta-2,4-dienoate (6.0 g, 61.1 mmol) in dry diethyl ether (90 cm^3) was added dropwise to a suspension of lithium aluminium hydride (1.2 g, 31.6 mmol) in dry ether under nitrogen at −5 °C. After stirring at room temperature for 1 h water was carefully added to destroy the excess of lithium aluminium hydride. The ether layer was decanted, and conc. HCl was added to the aqueous layer, which was subsequently extracted with more ether. The combined ether layers were washed with water, dried (Na$_2$SO$_4$) and distilled to yield a mixture of (*E*)- and (*Z*)-3-methylpenta-2,4-dien-1-ol (3.42 g, 57%), b.p. 88 °C/14 Torr (lit.,[33] 75–76 °C/15 Torr). The NMR spectra of the *E*- and *Z*-isomers overlapped to some extent, but agreed with the literature.[35]

5-*Bromo*-3-*methylpenta*-1,3-*diene*.[36]—Phosphorus tribromide (1.1 g, 4.1 mmol) was added dropwise to a solution of 3-methylpenta-2,4-dien-1-ol (1.0 g, 10.2 mmol) and pyridine (0.04 g, 0.51 mmol) in dry diethyl ether (20 cm^3) cooled to −5 °C in an ice/salt bath. The mixture was stirred while cold for 20 min then ice/water (20 cm^3) was added. The ether was decanted and the aqueous phase was extracted with more ether. The combined ether layers were washed (water, sat. NaHCO$_3$, sat. NaCl), dried (Na$_2$SO$_4$) and distilled to give (*E*)- and (*Z*)-5-bromo-3-methylpenta-1,3-diene (0.75 g, 45%), b.p. 52 °C/14 Torr (lit.,[36] 45 °C/10 Torr). The ^{1}H NMR spectra overlapped considerably but were in good agreement with the literature.

3,8-*Dimethyldeca*-1,3,7,9-*tetraene* (**16**) *and Isomers*.—A portion of a solution of 5-bromo-3-methylpenta-1,3-diene (4.0 g, 24.8 mmol) in dry diethyl ether (100 cm^3) was added to dry magnesium turnings (0.8 g, 32.9 mmol) and a crystal of iodine, under nitrogen. The mixture was heated gently to start the reaction and the remainder of the bromide was added at such a rate as to maintain gentle reflux. Reflux was then continued for a further 1.5 h. Copper(I) chloride (0.3 g) and 5-bromo-3-methylpenta-1,3-diene (4.0 g, 24.8 mmol) in dry ether (50 cm^3) were added and the mixture was refluxed for 5 h. The solution was cooled, poured onto cold NH$_4$Cl solution (100 cm^3), extracted with ether (×3). The combined ether layers were washed with water, dried (Na$_2$SO$_4$) and distilled to give a mixture of C$_{12}$H$_{18}$ isomers (3.1 g, 77%), b.p. 50 °C/1 Torr, which were separated by preparative gas chromatography (2 m column packed with 20% Carbowax 20M at 115 °C). Peak 1: (*Z*)-3,6-dimethyl-6-vinylocta-1,3,7-triene (**19**) (1.6%); δ_H 1.09 (3 H, s, CH$_3$), 1.84 (3 H, s, CH$_3$), 2.29 (2 H, d, CH$_2$), 4.94–5.10 (7 H, m), 5.82 (2 H, dd), 6.74 (1 H, dd, CH). Peak 2: (*E*)-3,6-dimethyl-6-vinylocta-1,3,7-triene (**18**) (21.9%); δ_H 1.08 (3 H, s, CH$_3$), 1.74 (3 H, s, CH$_3$), 2.27 (2 H, d, CH$_2$), 4.91–5.12 (6 H, m), 5.46 (1 H, t, CH), 5.82 (2 H, dd), 6.37 (1 H, dd, CH); δ_C 12.00 (CH$_3$), 23.03 (CH$_3$), 39.15 (CH$_2$), 43.77 (C), 110.30 (CH$_2$), 112.36 (CH$_2$), 129.27 (CH), 135.70 (C), 141.82 (CH), 145.52 (CH); *m*/*z* (%) 162 (M$^+$, 1), 147 (4), 133 (1), 119 (2), 106 (4), 91 (3), 81 (100), 79 (46), 77 (11), 65 (9), 53 (37), 41 (44). Peak 3: (*Z*),(*E*)-3,8-dimethyldeca-1,3,7,9-tetraene (**17**) (10.6%); δ_H 1.73 (3 H, s, CH$_3$), 1.82 (3 H, s, CH$_3$), 2.25 (4 H, m), 5.01 (2 H, dd, CH_2), 5.16 (2 H, dd, CH_2), 5.40 (1 H, br t, CH), 5.49 (1 H, br t, CH), 6.37 (1 H, dd, CH), 6.77 (1 H, dd, CH); δ_C 11.67 (CH_3), 19.55 (CH_3), 27.16 (CH_2), 28.36, (CH_2), 110.66 (CH_2), 113.52 (CH_2), 130.54 (CH), 132.39 (CH), 133.58 (C), 134.66 (C), 141.79 (CH). Peak 4: (*E*),(*E*)-3,8-dimethyldeca-1,3,7,9-tetraene (**16**) (65.9%); δ_H 1.74 (6 H, s, 2 × CH_3), 2.24 (4 H, m, 2 × CH_2), 5.01 (4 H, dd, 2 × CH_2), 5.48 (2 H, br t, CH), 6.36 (2 H, dd, CH); δ_C 11.43 (CH_3), 28.18 (CH_2), 110.60 (CH_2), 132.09 (CH), 134.18 (C), 141.31 (CH); *m/z* (%) 162 (M^+, 5), 147 (4), 133 (2), 119 (3), 106 (10), 91 (4), 81 (100), 79 (51), 77 (14), 65 (13), 53 (51), 41 (67).

2,6-*Dimethylhepta*-3,5-*dien*-4-*ol* (**21**).—To a solution of lithium aluminium hydride (1.5 g, 39.5 mmol) in dry diethyl ether (150 cm^3) at 0 °C under nitrogen, a solution of 2,6-dimethylhepta-2,5-dien-4-one (phorone) (15.0 g, 109 mmol) in dry ether (100 cm^3) was added dropwise. The suspension was stirred overnight at room temperature. The excess of lithium aluminium hydride was cautiously decomposed by addition of water and the clear ether layer was removed. The moist ether layer was treated with dil. HCl and re-extracted with ether (2 × 100 cm^3). The combined ether layers were washed (sat. $NaHCO_3$, water), dried (Na_2SO_4) and distilled to give **21** as a clear, colourless liquid (6.0 g, 39%). The NMR spectra were in good agreement with the literature.[37]

Reaction of **21** *with McMurray's Reagent*.—Titanium(III) chloride (26.29 g, 17 mmol) and lithium aluminium hydride (2.17 g, 57 mmol) were stirred in dry dimethoxyethane (100 cm^3) for 30 min. A solution of 2,6-dimethylhepta-2,5-dien-4-ol (8.0 g, 57 mmol) in dry dimethoxyethane (40 cm^3) was added dropwise to the slurry and the resulting mixture was refluxed for 24 h under nitrogen. After cooling, water (100 cm^3) was cautiously added and the mixture was extracted with diethyl ether (3 × 100 cm^3). The combined ether layers were washed (water, sat. NaCl) dried (Na_2SO_4), and distilled to give a pale yellow liquid (b.p. 40 °C/1 Torr) in low yield. The spectral data showed that the major component of this liquid was not the expected symmetrical dimer **22**, but was instead 2,6,6,9-tetramethyl-7-(2-methylprop-1-enyl)deca-2,4,8-triene (**23**); δ_H 0.94 (6 H, s, 2 × CH_3), 1.59 (6 H, s, 2 × CH_3), 1.68 (6 H, s, 2 × CH_3), 1.77 (6 H, s, 2 × CH_3), 2.95 (1 H, t, CH), 5.00 (2 H, d, 2 × CH), 5.60 (1 H, d, CH), 5.70 (1 H, d, CH), 6.10 (1 H, dd, CH); δ_C 18.29 (CH_3), 18.36 (CH_3), 25.44 (CH_3), 25.96 (CH_3), 26.12 (CH_3), 40.49 (C), 47.49 (CH), 123.14 (CH), 125.44 (CH), 125.73 (CH), 130.81 (C), 132.56 (C), 140.22 (CH); *m/z* (%) 246 (M^+, 10), 190 (5), 149 (5), 123 (52), 107 (47), 81 (29), 69 (100). Attempts to separate the product mixture by preparative gas chromatography were frustrated by the viscous, high boiling nature of the components.

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