# The Electron Spin Resonance Spectra of the Penta-alkylcyclopentadienyl Radicals MeR$_4$C$_5$· (R = Et, Pr, and Bu) and 1,3,5-Me$_3$-2,4-Et$_2$C$_5$·. Relative Substituent Effects of the Alkyl Groups

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The penta-alkylcyclopentadienyl radicals Me$_4$EtC$_5$·, Me$_4$PrC$_5$·, Me$_4$BuC$_5$·, and 1,3,5-Me$_3$-2,4-Et$_2$C$_5$· have been prepared by photolysis of the corresponding penta-alkylcyclopentadienes. The e.s.r. spectra which are observed are strongly temperature-dependent. It is assumed that the unsymmetrical penta-alkylation breaks the degeneracy of the ψ_A and ψ_S molecular orbitals of the cyclopentadienyl radical, and that there is a Boltzmann distribution of the unpaired electron between these two levels. The e.s.r. spectra which are observed then represent a population-weighted average of the spectra associated with the radical in the $\psi_A{}^1\psi_S{}^2$ and $\psi_S{}^2\psi_A{}^1$ configurations. The McLachlan equation is used to give the spin-density distributions in these two configurations, and the induced separation between the ψ_A and ψ_S energy levels can then be derived. It is concluded that in the π-radical R–Ċ$\subset$, the relative electron-releasing interaction between the alkyl group R and a unit p-electron on the attached carbon atom falls in the sequence (kJ mol^{-1}) Me (0) > Et (1.79) ~ Pr (1.84) ~ Bu (1.99).

WE have shown recently that when 1,2,3,4,5-penta-methylcyclopentadiene (IH) is irradiated with u.v. light, hydrogen is evolved and the e.s.r. spectrum of the pentamethylcyclopentadienyl radical (I) is observed. The reaction apparently involves the unimolecular homolysis of the ring C–H bond as shown in Scheme 1.[1]
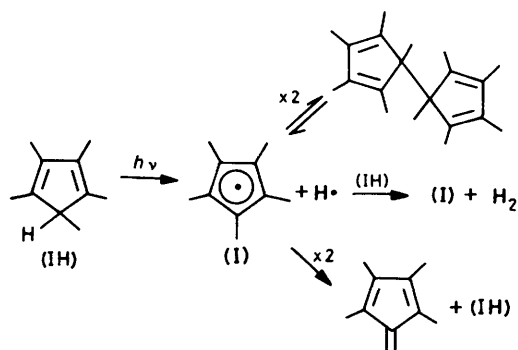
SCHEME 1

Such photosensitivity is unprecedented in a hydro-carbon. We have found that it extends to a variety of functionally substituted derivatives of pentamethyl-cyclopentadienes, Me$_5$C$_5$X, where it promises to provide a source of various hetero-centred radicals, X·.[2]

It was interesting for a variety of reasons to study the photolysis of other penta-alkylcyclopentadienes. First, any dependence of the photosensitivity on the nature of the substituents might provide evidence regarding the origin of the effect. Secondly, tetramethyl(ethyl)-cyclopentadiene is more readily accessible than penta-methylcyclopentadiene, which would be important particularly if the functionally substituted derivatives are to be used as a source of hetero-radicals, X·. Most important, we hoped that it might be possible to inter-pret the e.s.r. spectra of the cyclopentadienyl radicals with mixed alkyl groups in terms of the differential interaction of the different alkyl groups upon the π-electron system, on the model which we have followed for the partially methylated cyclopentadienyl radicals,[3] and thereby provide a new method for measuring substituent effects.

This last point is our particular interest in this paper. We report an e.s.r. study of the photolysis of the penta-alkylcyclopentadienes, 1,2,3,4-Me$_4$-5-RC$_5$H, where R = Et, Pr, and Bu, and 1,3,5-Me$_3$-2,4-Et$_2$C$_5$H, and the interpretation of the spectra which are observed in terms of Hückel molecular orbital theory.

DISCUSSION

Preparation of the Penta-alkylcyclopentadienes.—The mixed alkylcyclopentadienes (IIH)—(VH) were prepared as shown in Schemes 2 and 3. Tetramethyl(ethyl)-cyclopentadiene has been prepared previously by the method shown in Scheme 2, though using methyl-lithium rather than methylmagnesium iodide,[4] and tetramethyl(propyl)- and tetramethyl(butyl)-cyclopenta-diene have been prepared from the dehydrative ring-
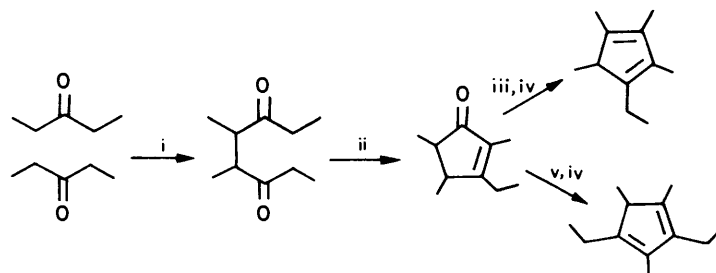

SCHEME 2 *Reagents:* i, PbO$_2$; ii, KOH; iii, MeMgI; iv, I$_2$; v, EtMgI
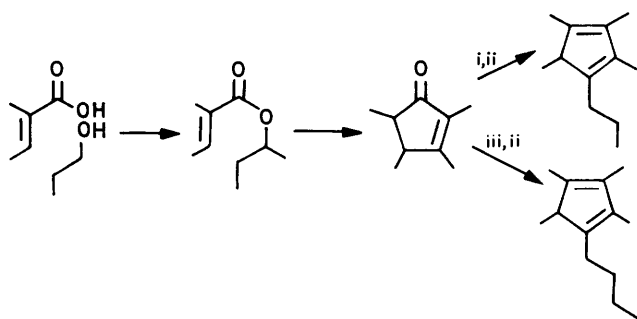
SCHEME 3 i, PrMgI; ii, I$_2$; iii, BuMgI

closure of the appropriate 4-alkyl-3,5-dimethylhepta-2,5-dien-4-ol.[5] The trimethyl(diethyl)cyclopentadiene (IIIH) does not appear to have been reported.

Photolysis of the Penta-alkylcyclopentadienes.—The hydrocarbons (IIH)—(VH) were photolysed in cyclopropane or toluene solution in the cavity of an e.s.r.

(II)   (III)   (IV)   (V)
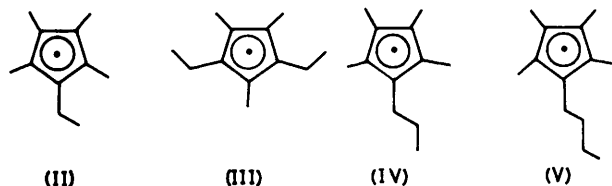
spectrometer between *ca.* −140 and 100 °C. Bubbles of hydrogen were continuously evolved during the photolysis, and strong spectra of the corresponding penta-alkylcyclopentadienyl radicals (II)—(V) were observed.

The spectra were strongly temperature-dependent, and they were analysed by computer simulation. Typical experimental and simulated spectra at two temperatures are given for the radicals (II)—(V) in Figures 1—4.

The results are given in Tables 1—4, where the measured values of the hyperfine coupling constants, *a*, appear in columns 2, 4, and 9.

Analysis of the Results.—Details of the way in which the results are analysed are given in our preceding paper.[3] Spin densities, ρ, in the ψ_A and ψ_S MOs of the cyclopentadienyl system are calculated from the Hückel coefficients by the McLachlan equation. The value of λ is chosen to be 0.75 to accommodate the maximum spectral width for substituted cyclopentadienyl radicals (*viz.* MeC$_5$H$_4$·, 1,5-Me$_2$C$_5$H$_3$·, 1,3,4-Me$_3$C$_5$H$_2$·, Cl$_3$SiC$_5$H$_4$·, and indenyl·).[3] If the McConnell Q_{Me} constant for the Me$_5$C$_5$· radical in both the ψ_A and ψ_S configurations is taken to be 31.85 G, as we have argued,[3] the predicted values for the proton hyperfine coupling constants, a_{iA} and a_{iS}, for the Me$_5$C$_5$· radical in the ψ_A and ψ_S configurations can then be calculated from the McConnell equation.

For equilibration between the two MOs, with the populations P_A and P_S ($P_A + P_S = 1$), the predicted resultant values of a_i are then given by equation (1).

$$a_i = P_A a_{iA} + P_S a_{iS} \qquad (1)$$

If the appropriate values of a_{iA} and a_{iS} (from the McLachlan equation, in units of gauss) are introduced, equation (1) gives, on rearrangement, (2)—(4).
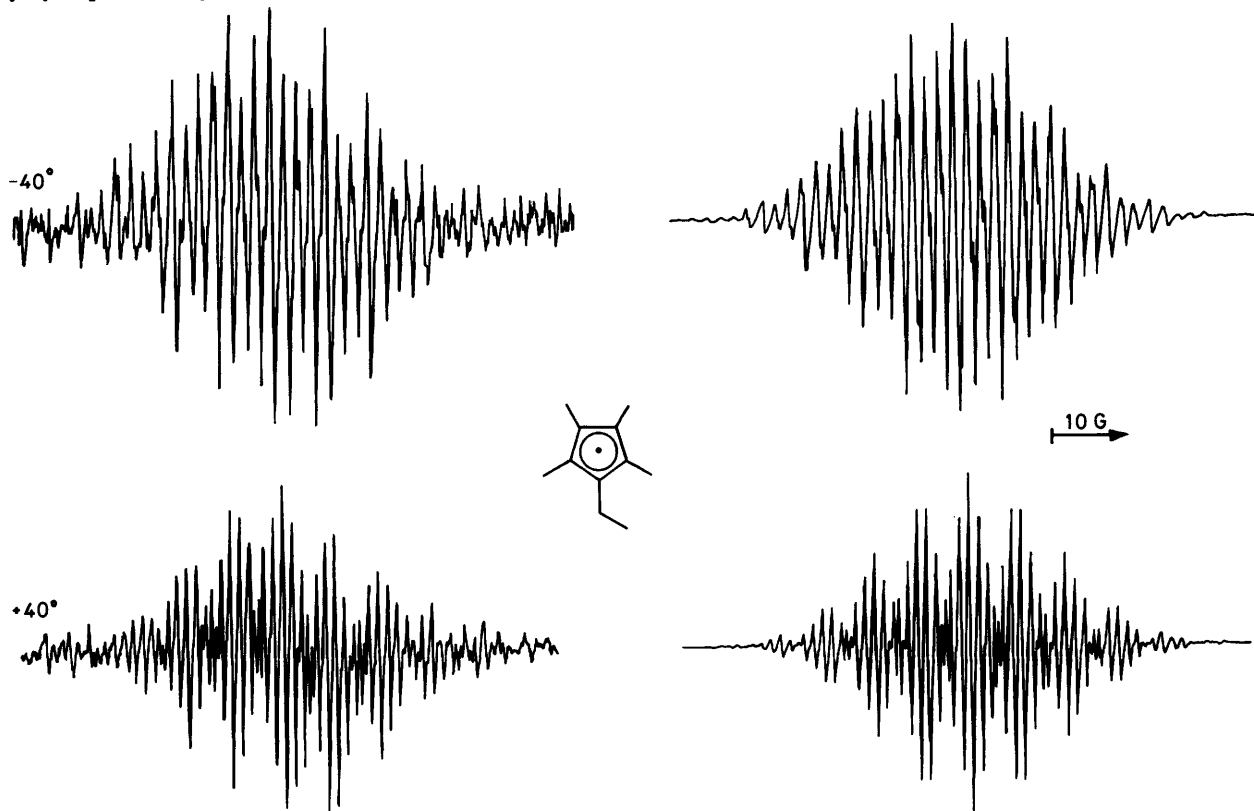

FIGURE 1   E.s.r. spectrum, and simulation, of the radical Me$_4$EtC$_5$· at −40 and 0 °C

$$P_A = (15.51 - a_1)/17.70 \qquad (2)$$
$$= (a_{2,5} + 1.03)/14.42 \qquad (3)$$
$$= (9.21 - a_{3.4})/5.56 \qquad (4)$$

Columns 3 and 5 of Tables 1—4 give the values of P_A calculated by equations (2)—(4) from the hyperfine coupling constants in the immediately preceding columns, and these two derived populations are averaged in column 6.

The concept of the hyperfine coupling (a^*) to an imaginary proton at a ring-substituted position is often a useful one. It is usually derived on the basis of the assumption that the sum of the hyperfine coupling constants, real and imaginary, is equal to Q whatever
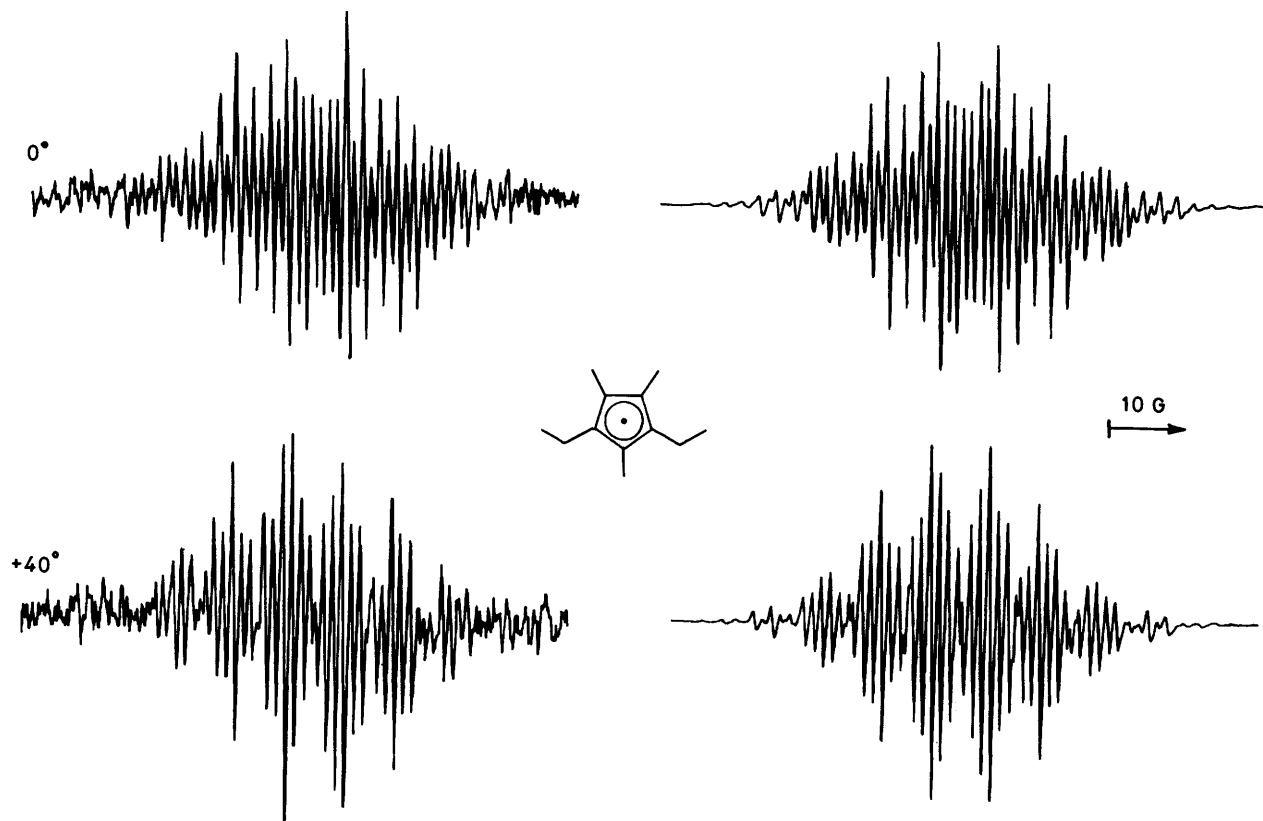

FIGURE 2   E.s.r. spectrum, and simulation, of the radical $Me_3Et_2C_5{}^\bullet$ at 0 and +40 °C

TABLE 1

Temperature dependence of the e.s.r. spectrum of the radical $Me_4EtC_5{}^\bullet$

$T/°C$	$a_{2,5}/G$	P_A	$a_{3.4}/G$	P_A	P_A	$a_1{}^*/G$	$\ln \bar{P}_8/\bar{P}_A$	$a(CH_2)/$ G	$a(CH_3)$, $\rho = 1/G$
−133	8.50	0.643	5.55	0.647	0.645	3.72	−0.597	1.66	14.21
−114	8.22	0.624	5.65	0.629	0.627	4.06	−0.519	1.82	14.32
−73	7.79	0.595	5.76	0.610	0.603	4.49	−0.418	2.01	14.27
−32	7.51	0.576	5.85	0.594	0.585	4.82	−0.343	2.22	14.68
+10	7.33	0.564	5.95	0.576	0.570	5.09	−0.282	2.42	15.14
+47	7.17	0.553	5.99	0.569	0.561	5.26	−0.245	2.60	15.76
+87	7.03	0.544	6.01	0.565	0.555	5.36	−0.221	2.74	16.27
+107	6.98	0.540	6.02	0.564	0.552	5.42	−0.209	2.80	16.45

TABLE 2

Temperature dependence of the e.s.r. spectrum of $Me_3Et_2C_5{}^\bullet$

| $T/°C$	a_1/G	P_A	$a_{3.4}/G$	P_A	$\bar{P}_A$	$a_{2.5}{}^*/G$	$\ln \bar{P}_8/\bar{P}_A$	$a(CH_2)/$ G	$a(CH_3)$, $\rho = 1/G$
−133	10.15	0.293	7.48	0.306	0.299	3.40	0.852	1.41	13.19
−114	9.70	0.318	7.33	0.332	0.325	3.79	0.731	1.57	13.19
−73	9.16	0.348	7.10	0.378	0.361	4.31	0.571	1.78	13.16
−32	8.56	0.380	7.00	0.390	0.385	4.68	0.468	2.04	13.89
+10	8.21	0.399	6.90	0.408	0.404	4.96	0.389	2.23	14.32
+47	8.00	0.411	6.78	0.429	0.420	5.20	0.323	2.48	15.20
+87	7.76	0.424	6.71	0.442	0.433	5.39	0.270	2.60	15.36
+107	7.62	0.432	6.65	0.452	0.442	5.52	0.233	2.70	15.57
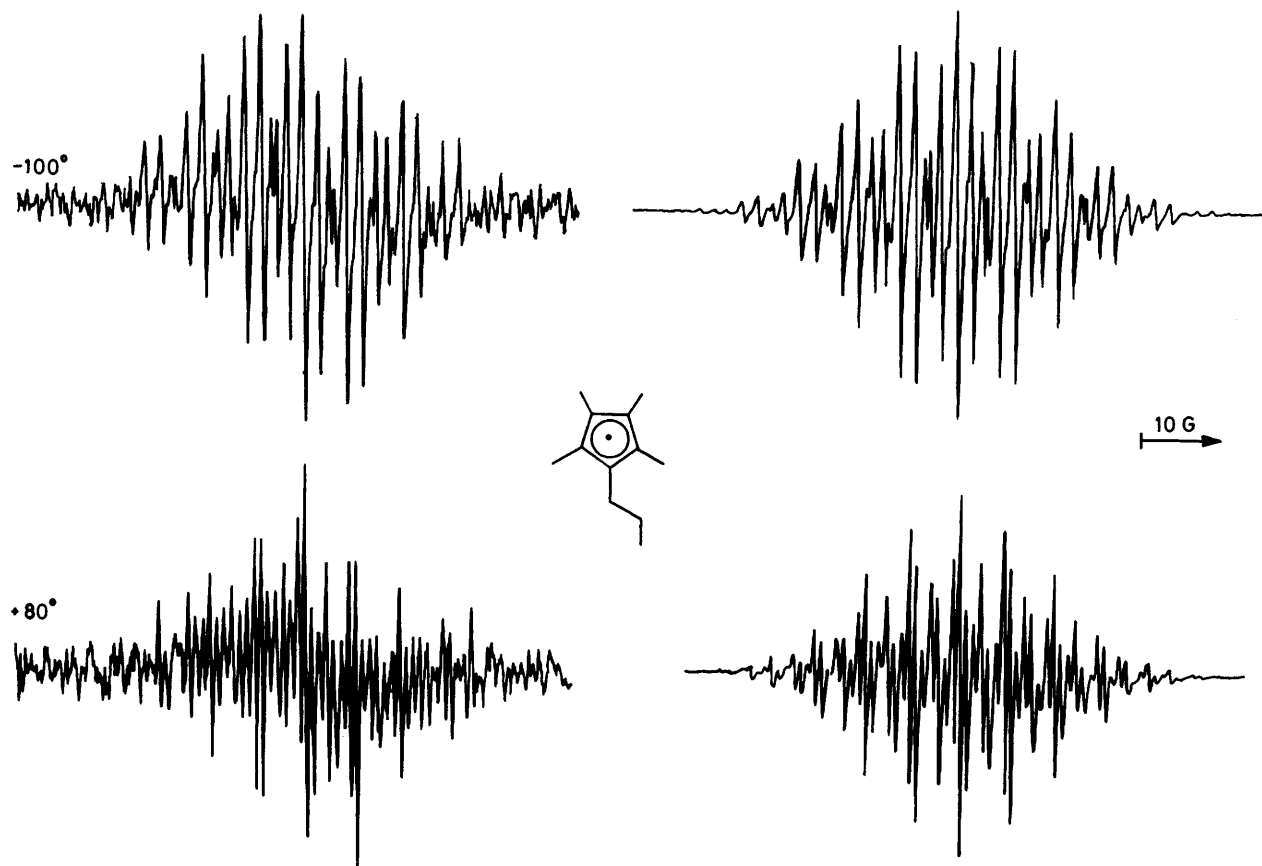
FIGURE 3 E.s.r. spectrum, and simulation, of the radical $Me_4PrC_5^{\cdot}$ at -40 and $+40$ °C

the value of P_A and P_S. We maintain, however, that the spectral width increases as P_A and P_S deviate from 0.5;[3] therefore we have derived values of a^* from the general equation (5), whence comes (6) and (7). The

$$a_i = (P_A\rho_{iA} + P_S\rho_{iS})Q_{Me} \qquad (5)$$

$$a_1^* = 15.51 - 18.28P_A \qquad (6)$$

$$a_{2.5}^* = 14.82P_A - 1.03 \qquad (7)$$

calculated values of a_1^* or $a_{2.5}^*$ are listed in column 7 of Tables 1—4.

On the model of thermal population of the ψ_A and ψ_S MOs, the populations should be related to the separation in energy induced between ψ_A and ψ_S, by the Boltzmann equation (8).

$$\ln(P_S/P_A) = -\Delta E/RT \qquad (8)$$

Figure 5 illustrates plots of $\ln(P_S/P_A)$ against $1/T$, and the derived values of ΔE are given in Table 5.

Column 10 of Tables 1—4 gives the measured values of the hyperfine coupling constants of the methylene group by which the ethyl, propyl, or butyl substituent is connected to the cyclopentadienyl ring. To remove the effects of the differing populations of the ψ_A and ψ_S orbitals, these values of $a(CH_2)$ are normalised in column 10 to unit spin density on the α(ring) carbon atom, using equations (11) and (12).

$$\rho_i = P_A\rho_{iA} + P_S\rho_{iS} \qquad (9)$$

$$a_i(CH_2)\ (\rho = 1) = a_i(CH_2)/\rho_i \qquad (10)$$

$$a_1(CH_2)\ (\rho = 1) = \frac{a_1(CH_2)}{0.4869 - 0.5738P_A} \qquad (11)$$

$$a_{2.5}(CH_2)\ (\rho = 1) = \frac{a_{2.5}(CH_2)}{0.4652P_A - 0.0322} \qquad (12)$$

TABLE 3

Temperature dependence of the e.s.r. spectrum of the radical $Me_4PrC_5^{\cdot}$

$T/°C$	$a_{2,5}/G$	P_A	$a_{3,4}/G$	P_A	$\bar{P}_A$	a_1^*/G	$\ln\bar{P}_S/\bar{P}_A$	$a(CH_2)/$ G	$a(CH_2)$, $\rho = 1/G$
−133	8.32	0.631	5.60	0.638	0.635	3.90	−0.554	1.76	14.36
−93	8.14	0.619	5.68	0.624	0.621	4.14	−0.458	1.88	14.46
−74	7.90	0.602	5.72	0.617	0.610	4.36	−0.447	2.05	14.98
−33	7.61	0.583	5.79	0.604	0.594	4.65	−0.381	2.22	15.20
+7	7.43	0.571	5.86	0.592	0.581	4.87	−0.331	2.42	15.82
+26	7.35	0.565	5.92	0.581	0.574	5.02	−0.298	2.52	16.00
+47	7.25	0.559	5.95	0.576	0.568	5.13	−0.274	2.63	16.34
+87	7.15	0.552	5.98	0.571	0.562	5.24	−0.249	2.68	16.30
+107	7.12	0.550	6.01	0.566	0.558	5.31	−0.233	2.77	16.61
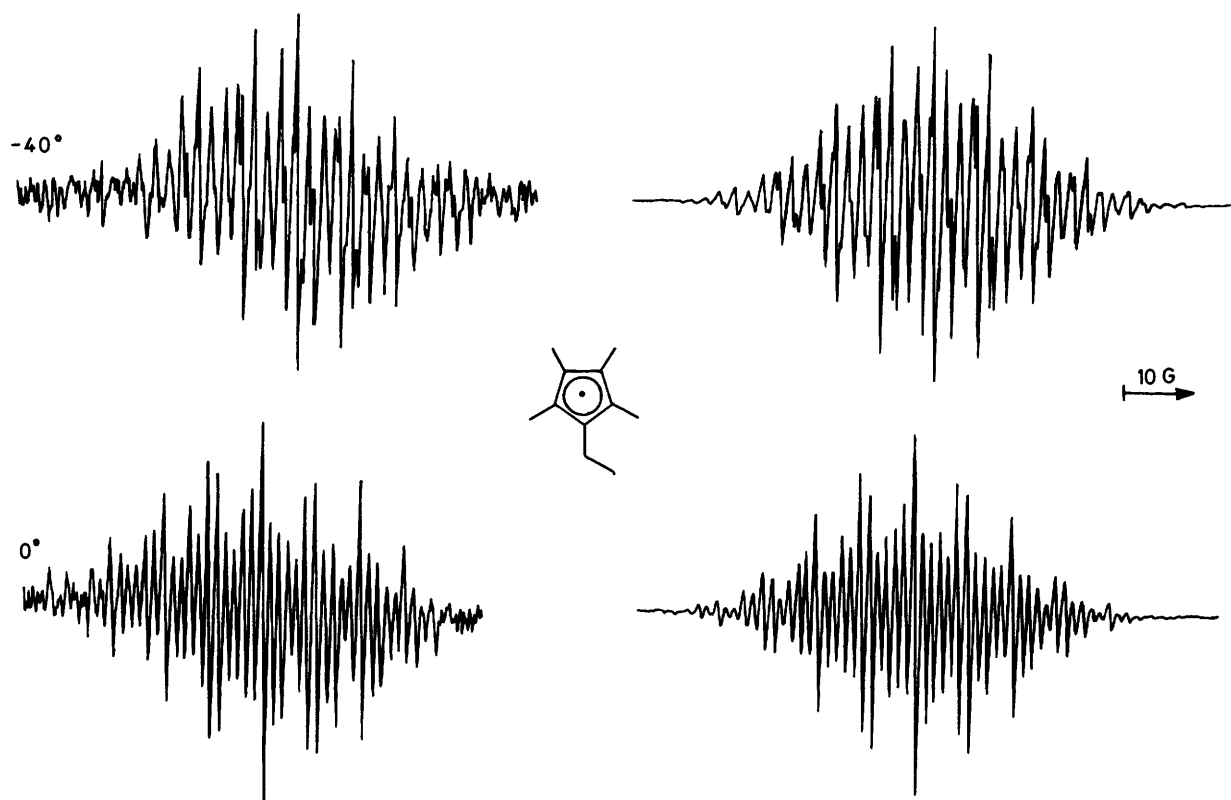
FIGURE 4   E.s.r. spectrum, and simulation, of the radical $Me_4BuC_5\cdot$ at -100 and $+80$ °C

TABLE 4

Temperature dependence of the e.s.r. spectrum of $Me_4BuC_5\cdot$

$T/°C$	$a_{2,5}/G$	P_A	$a_{3,4}/G$	P_A	$\bar{P}_A$	a_1*/G	$\ln\bar{P}_S/\bar{P}_A$	$a(CH_3)/$ G	$a(CH_2)$ $\rho = 1/G$
-113	8.14	0.618	5.63	0.633	0.626	4.07	-0.515	1.90	14.88
-103	8.02	0.610	5.67	0.626	0.619	4.20	-0.485	1.96	14.88
-93	7.92	0.604	5.70	0.621	0.613	4.30	-0.460	2.02	14.95
-73	7.75	0.592	5.76	0.610	0.601	4.52	-0.410	2.10	14.78
-53	7.56	0.579	5.92	0.599	0.589	4.74	-0.360	2.23	14.97
-34	7.40	0.569	5.86	0.592	0.581	4.89	-0.327	2.40	15.63
$+7$	7.23	0.557	5.93	0.580	0.569	5.11	-0.278	2.55	15.90
$+47$	7.04	0.544	6.02	0.564	0.554	5.38	-0.217	2.74	16.21
$+87$	6.96	$\cdot$ 0.539	6.06	0.557	0.548	5.49	-0.193	2.87	16.64
$+107$	6.89	0.534	6.10	0.550	0.542	5.60	-0.168	2.92	16.60

It should be pointed out that the best straight lines drawn for the Boltzmann plots (Figure 5) show small intercepts on the axes, whereas according to equation (7), they should pass through the origin. The significance of this is not clear, but the same behaviour is apparent in other similar systems, notably Sakurai's work on the

TABLE 5

Splitting of the degeneracy of the molecular orbitals of the $C_5H_5\cdot$ radicals

Radical	$\Delta E/$ kJ mol^{-1}	δq	$\kappa_R^{Me}/$ kJ mol^{-1}
$Me_4EtC\cdot$	$+0.72$	-0.400	$+1.79$
$1,3,4$-Me_3-$2,5$-$Et_2C_5\cdot$	-1.11	$+0.650$	$+1.71$
$Me_4PrC\cdot$	$+0.74$	-0.400	$+1.84$
$Me_4BuC\cdot$	$+0.79$	-0.400	$+1.99$

monosilylated cyclopentadienyl radicals,[6] and Möbius' work on the methylated pentaphenylcyclopentadienyl radicals.[7]

Interaction Energy of the Alkyl Substituents.—From the slopes of the Boltzmann plots in Figure 5, the energy separations, ΔE, between the ψ_A and ψ_S MOs induced by the unsymmetrical penta-alkylation of the ring can be derived. The results are given in Table 5.

To normalise the effect of the substituent to unit net difference in electron density at the positions of substitution, j, between the ψ_A and ψ_S MOs, we make use of the interaction factors, κ_R^{Me}, defined by equation (13).

$$\Delta E = \kappa_R^{Me}(\Sigma q_{jA} - \Sigma q_{jS}) \qquad (13)$$

$$= \kappa_R^{Me}\delta q \qquad (14)$$

Values of δq and of the derived values of κ_R^{Me} are given in Table 5.

If the effects of the substituents are additive, these interaction factors should be constant for a given alkyl group. For the radical $Me_4EtC_5{}^\bullet$, the results show that, compared with a methyl group, the ethyl group destabilises a single electron in ψ_S with respect to ψ_A by
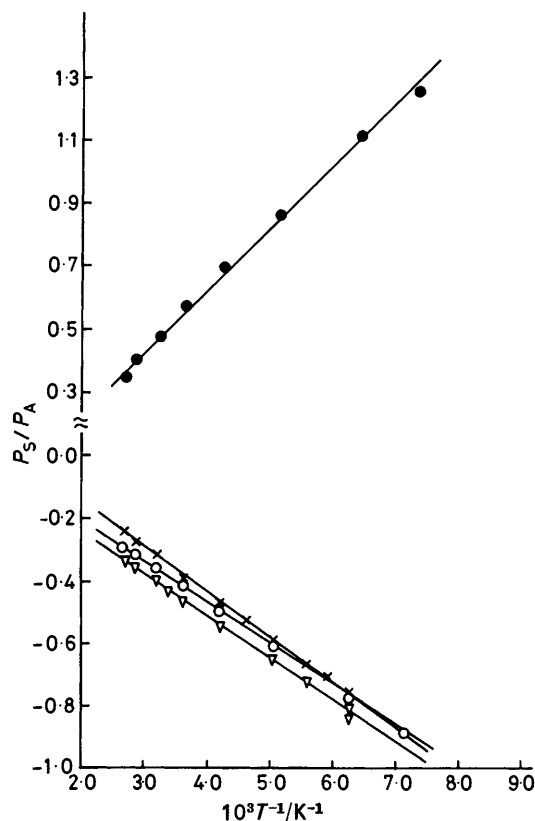

FIGURE 5 Boltzmann plots of the relative populations of the ψ_S and ψ_A MOs of the radicals $\bigcirc$ $Me_4EtC_5{}^\bullet$, $\bullet$ $Me_3Et_2C_5{}^\bullet$, $\bigtriangledown$ $Me_4PrC_5{}^\bullet$, and $\times$ $Me_4BuC_5{}^\bullet$

0.72 kJ mol^{-1}, or 1.79 kJ mol^{-1} for unit π-electron density on the α-carbon atom. For the radical $Me_3Et_2C_5{}^\bullet$ ψ_S is now *stabilised* with respect to ψ_A by 1.1 kJ mol^{-1}, implying than an ethyl group repels electrons less strongly than methyl by 1.71 kJ mol^{-1} per unit π-electron. The reasonable agreement between these two values of κ_{Et}^{Me} is encouraging.

The values of κ_{Pr}^{Me} of -1.84 kJ mol^{-1}, and of κ_{Bu}^{Me} of -1.99 kJ mol^{-1}, imply that the electron-releasing effect may decrease further in the sequence Et > Pr > Bu. We hope to test this, and to check the method further for internal consistency, by examining the radicals $Et_5C_5{}^\bullet$, $Et_4PrC^\bullet$, and $Et_4BuC^\bullet$.

The sequence of electron releasing power which we derive (Me > Et $\sim$ Pr $\sim$ Bu) is the same as that [Me > Et (>Pr^i > Bu^t)] which Sakurai inferred from the small differences in $a_1{}^*$ values observed for the various monoalkylcyclopentadienyl radicals,[8] which Jones derived from the temperature-dependence of the e.s.r. spectra of the alkylbenzene radical anions,[9] and

which de Boer and Colpa obtained from an n.m.r. study of the p-alkyl-substituted toluene radical anions.[10] It is also in accord with the substituent effect on the σ^+ and $\Delta\sigma_R$ ($= \sigma^+ - \sigma^n$) scales [σ^+ Me -0.32, Et -0.31 (Pr^i -0.29, Bu^t -0.27)].[11] This sequence is not that which would be expected for the inductive effect; it suggests that the alkyl groups release electrons by σ–π hyperconjugation, the C–H bond being more effective than the C–C bond. This hyperconjugation manifests itself also in the hyperfine coupling to the methylene group by which the alkyl group is connected to the ring.

The Values of a($CH_{2\beta}$).—The low values of $a(CH_{2\beta})$ (Tables 1—4, final column) normalised to unit π-density at the α-carbon atom, and their positive temperature coefficients, imply that in all four radicals, the alkyl substituent is most stable in the conformation where the C_β–C bond eclipses the p-orbital on C_α, as shown in the Newman projection (VI).

(VI)   (VII)
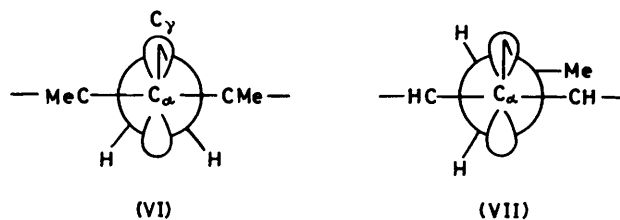
This is in contrast to the monoethylcyclopentadienyl radical, which shows $a(CH_{2\beta})$ *ca.* 15.8 G at -70 °C, or *ca.* 40.6 G when normalised to unit spin density, and a negative temperature coefficient, implying that C_γ now tends to lie in the plane of the ring, as in (VII), at low temperature.[8,12] This difference can presumably be ascribed to the steric effect of the methyl groups in $Me_4RC_5{}^\bullet$ and $Me_3Et_2C_5{}^\bullet$, which displace C_γ out of the plane of the ring.

The relative contributions of C–H and C–C hyperconjugation, and the resulting value of ΔE should therefore be temperature-dependent, but, if such an effect is present, it is too small to be detected in the Boltzmann plots.

It would obviously be interesting in this context to study the behaviour of the radicals $Me_4Pr^iC_5{}^\bullet$ and $Me_4Bu^tC_5{}^\bullet$, but our initial attempts to prepare their precursors have been unsuccessful. At low temperature, the C_β–H bond of the isopropyl group should lie in the plane of the ring, and, if C–H hyperconjugation is more important than C–C hyperconjugation, both the isopropyl and t-butyl groups should show similar low interaction factors κ_R^{Me}.

EXPERIMENTAL

The final stage of the preparation of the penta-alkylcyclopentadienes involved the dehydration of the corresponding 1,2,3,4,5-penta-alkylcyclopent-2-enols with iodine. Analysis of the products by g.l.c.–m.s. showed the presence of two isomers with the appropriate molecular mass, which appear to be the cyclopentadiene and the corresponding 3-alkylidenecyclopentene. The percentage of this second isomer was *ca.* 5 for (IIH), 10 for (IIIH), 80

for (IVH), and 95 for (VH), but its presence did not complicate the photolysis of the cyclopentadiene, nor the interpretation of the e.s.r. spectra of the cyclopentadienyl radicals. The dehydration of 2,3,4-trimethylcyclopent-2-enol under a variety of conditions has similarly been shown to give up to 30% of the 3-methylenecyclopentene.

1-*Ethyl-2,3,4,5-tetramethylcyclopentadiene*.—3-Ethyl-2,4,5-trimethylcyclopent-2-enone was prepared from pentan-3-one by Feitler and Whitesides' method,[4] then treated with methylmagnesium iodide in ether to give the alcohol, which was dehydrated with iodine,[4] yielding ethyltetramethyl-cyclopentadiene as a yellow oil (61%), b.p. 60—62 °C at 5 mmHg (lit., 59—61 °C at 5 mmHg), δ(CDCl$_3$) 2.30 (2 H, m, CH_2CH$_3$), 1.85 (3 H, s, Me), 1.82 (3 H, s, Me), 1.80 (3 H, s, Me), 1.75 (1 H, m, CH), 1.05 (3 H, t, CH$_2$CH_3), and 1.00 (3 H, d, CHCH_3).

1,3-*Diethyl-2,4,5-trimethylcyclopentadiene*.—This was prepared as a yellow oil (50% yield), b.p. 72 °C at 5 mmHg, from a similar reaction with ethylmagnesium bromide, δ(CDCl$_3$) 2.25 (2 H, q, CH_2CH$_3$), 1.85 (3 H, s, Me), 1.70 (1 H, m, CH), 1.10 (6 H, t, CH$_2$CH_3), and 1.0 (3 H, d, CHCH_3).

1,2,3,4-*Tetramethyl-5-propylcyclopentadiene*.—1,2,3,4-Tetramethylcyclopent-2-enone was prepared from 1-methyl-propyl tiglate in 33% yield.[4] This was treated with propyl-magnesium iodide in ether, and the resulting alcohol was dehydrated with iodine to give the tetramethylpropyl-cyclopentadiene (42%) as a yellow oil, b.p. 78 °C at 5 mmHg, δ(CDCl$_3$) 2.20 (2 H, m, CH_2CH$_2$CH$_3$), 1.80br (9 H, s, Me), 1.70 (1 H, m, CH), 1.20 (2 H, m, CH$_2$CH_2CH$_3$), 1.02 (3 H, t, CH$_2$CH$_2$CH_3), and 1.00 (3 H, m, CHCH_3).

1-*Butyl-2,3,4,5-tetramethylcyclopentadiene*.—This was prepared in 23% yield as a yellow oil, b.p. 86 °C at 5 mmHg, δ(CDCl$_3$) 2.20 (2 H, m, CH_2CH$_2$CH$_2$CH$_3$), 1.80br (9 H, s, 3 Me), 1.70 (1 H, m, CH), 1.22 (4 H, m, CH$_2$CH_2CH_2CH$_3$), 1.00 (3 H, d, CHCH$_3$), and 0.95 (3 H, t, CH$_2$CH$_2$CH$_2$CH_3).

E.s.r. Experiments.—Solutions of the hydrocarbons were prepared in cyclopropane under vacuum for experiments below 0 °C, or under nitrogen in toluene for experiments between 0 and 110 °C, and sealed in silica tubes, and photo-lysed in the cavity of a Varian E109 e.s.r. spectrometer with

light from a 500 W high pressure mercury arc, filtered through an aqueous solution of nickel and cobalt sulphates to remove i.r. radiation. Temperatures are probably accurate to ± 3 °C.

Products of Photolysis.—The products were analysed by g.l.c.–m.s. All showed the presence of the corresponding fulvenes. The products from Me$_4$BuC$_5$H (RH) showed a molecular ion for the dehydrodimer RR. The corresponding ion for the other three compounds could not be detected, but the fragment R indicated that the dehydro-dimer was present, and this was confirmed by the fact that thermolysis of the products at 90—110 °C, after photolysis, regenerated the e.s.r. spectrum of the radical R$^{\cdot}$.

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