The Photolysis of Cyclopentadienyl Compounds of Tin and Mercury. Electron Spin Resonance Spectra and Electronic Configuration of the Cyclopentadienyl, Deuteriocyclopentadienyl, and Alkylcyclopentadienyl Radicals

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Cyclopentadienyl derivatives of tin(IV) and mercury(II) and alkylcyclopentadienyl derivatives of mercury(II) are photolysed in solution to show the e.s.r. spectra of the appropriate radicals $RC_5H_4\cdot$ (R = H, D, Me, Et, Pr^i, or Bu^t). The $C_5H_5\cdot$ radical is a planar π-radical with average D_{5h} symmetry, and its spectrum is broadened in the presence of organic bromides, perhaps by a charge-transfer mechanism. The introduction of alkyl groups breaks the degeneracy of the ψ_A and ψ_S molecular orbitals of the π-system by electron release, destabilising the ψ_S MO, and the e.s.r. spectrum reflects the spin density distribution in the configuration $\psi_A{}^2\ \psi_S{}^1$. Deuterium has a small but detectable perturbing effect: the ψ_A MO is destabilised by *ca.* 100 J mol^{-1}, and thermal mixing of the two energy levels results in the configuration $\psi_S{}^{1.515}\ \psi_A{}^{1.485}$. This is compatible with the model of a vibrational perturbation of the resonance integral β, rather than of the Coulomb integral α.

LITTLE work has been reported on the photolysis of cyclopentadienylmetallic compounds, despite their importance in organometallic chemistry. The diamagnetic metallocenes $(\eta_5\text{-}C_5H_5)_2M$ (M = Fe, Ru, or Co^+) are photostable,[1] but the alkylmetallocenes $(\eta^5\text{-}C_5H_5)_2MR_2$ (M = Ti, Zr, and Hf) [2] and $(\eta^5\text{-}C_5H_5)_3ThR$ [3] undergo cleavage of the metal–alkyl bond, the group R producing alkane RH, or a spin adduct $Ra\cdot$ [4] or the end-group of a polymerized monomer, $RN_n\cdot$.[5] Paramagnetic metal-centred species have been detected where the metal is titanium, zirconium, and hafnium,[4] but there is good evidence that the cleavage of the Ti–Me bond does not liberate a free methyl radical.[5]

Pure $(\eta^5\text{-}C_5H_5)_2TiCl_2$ is not photosensitive, but the presence of impurities (perhaps HCl) promotes photodecomposition. Under these conditions, nitrosodurene shows the formation of the cyclopentadienyl spin adduct, but the free cyclopentadienyl radical has not been detected directly.[6]

We are not aware of any reports of the photolysis of cyclopentadienyl compounds of the main group metals. We report here an e.s.r. study of the photolysis of cyclopentadienyl and substituted cyclopentadienyl derivatives of tin(II), tin(IV), mercury(II), and lithium. In contrast to the derivatives of the transition metals described above (except perhaps titanocene dichloride [6]) these compounds undergo homolysis of the cyclopentadienyl–metal bonds to give the corresponding cyclopentadienyl and metallyl radicals [equation (1)].[7]

$$RC_5H_4M \xrightarrow{h\nu} RC_5H_4\cdot + M\cdot \qquad (1)$$
$$(R = H, D, \text{alkyl } etc.)$$

These reactions make it possible to study the e.s.r. spectra of substituted cyclopentadienyl radicals which have not been accessible previously. The spectra can be interpreted in terms of Hückel MO theory to provide evidence of the interaction of the substituents with the π-electron system of the ring,[8,9] and this is the focus of interest in the present paper. These reactions also provide a route to a series of novel tin-centred radicals $M\cdot$ ($M\cdot = R_nSnX_{3-n}$),[7] which will be described in a subsequent publication.

EXPERIMENTAL

Cyclopentadienes.—Cyclopentadiene and methylcyclopentadiene were prepared by thermal decomposition of the corresponding dimers, and ethyl-[10] and t-butyl-cyclopentadiene [11] by alkylation of cyclopentadienylsodium or cyclopentadienylmagnesium bromide with the appropriate alkyl bromide. Isopropylcyclopentadiene was obtained from the reaction of cyclopentadienylmagnesium bromide with isopropyl toluene-*p*-sulphonate.[12]

Cyclopentadienylmetallic Compounds.—Cyclopentadienyllithium was prepared by treating cyclopentadiene in ether with butyl-lithium (1.6M in hexane).

Ethylmagnesium bromide was treated with cyclopentadiene to give cyclopentadienylmagnesium bromide,[12,13] which reacted with cyclopentadienyl-lithium to give dicyclopentadienylmagnesium.[14]

Bis(cyclopentadienyl)mercury compounds $(RC_5H_4)_2Hg$ (R = H, Me, Et, Pr^i, and Bu^t), were prepared by lithiation of the appropriate cyclopentadiene in ether with butyllithium in hexane. Mercury(II) chloride was then added, and the lithium chloride which separated was filtered off. The solvent was removed, leaving the bis(cyclopentadienyl)mercury compound which was usually used for photolysis without further purification.[15] Alternatively, bis(cyclopentadienyl)mercury and bis(methylcyclopentadienyl)mercury were prepared on a larger scale by treating cyclopentadiene or methylcyclopentadiene with mercury(II) oxide in the presence of propylamine.[16]

A suspension of cyclopentadienyl-lithium (1.4 g) in ether (40 cm^3) was added dropwise with stirring to 2-chloro-1,3,2-dioxaborolane (2.0 g) at −40 °C under nitrogen. The solution was warmed to 0 °C, and stirred for 1 h. Lithium chloride was removed by filtration, and the solution of 2-(cyclopentadien-2-yl)-1,3,2-dioxaborolane was used for e.s.r. experiments without further purification; τ (Et_2O) 6.8 (2 H, s, cyclopentadienyl CH_2), 5.7 (4 H, s, OCH_2CH_2O), 3.0—3.5 (2 H, m, CH=CH), and 2.55 (1 H, s, CH=CB).[17] Tris(cyclopenta-2,3-dien-2-yl)borane was prepared from cyclopentadienyl-lithium and boron trichloride;[18] τ (Et_2O) 6.7 (2 H, s, CH_2), 3.0—3.5 (2 H, m, CH=CH), and 2.69 (1 H, s, CH=CB).

Cyclopentadienyltrimethylsilane, b.p. 140 °C, was prepared from cyclopentadienylsodium and trimethylchlorosilane.[19]

The following cyclopentadienyltin compounds were prepared similarly from cyclopentadienylsodium and the appropriate tin halide. $C_5H_5SnMe_3$, b.p. 80 °C at 10 mmHg,[20] $C_5H_5SnBu_3$, b.p. 90 °C at 0.005 mmHg;[20] $C_5H_5SnCl_3$;[21] $(C_5H_5)_2SnBu_2$, b.p. 126 °C at 0.1 mmHg;[20] $(C_5H_5)_2SnCl_2$, m.p. 38—40 °C;[20] $(C_5H_5)_3SnCl$, m.p. 45 °C;[20] $(C_5H_5)_4Sn$, m.p. 74 °C;[19,20] $(C_5H_5)_2Sn^{II}$, sublimes at 110 °C and 0.1 mmHg.[22] All showed satisfactory n.m.r. spectra and elemental analysis.

Hydrolysis of C_5H_5Li with D_2O gave C_5H_5D. This was treated with butyl-lithium then with tributyltin chloride to give a 1 : 1 mixture of $C_5H_5SnBu_3$ and $C_5H_4DSnBu_3$, b.p. 110—115 °C at 0.01 mmHg (*cf.* refs. 23 and 24).

Di(cyclopentadienyl)titanium dichloride was provided by Dr. R. J. H. Clark.

Tributyl(methylcyclopentadienyl)tin was prepared from methylcyclopentadienyl-lithium and tributyltin chloride following Davison and Rakita's general method;[24] τ (CCl_4) 4.20 (2 H), 4.48 (2 H), and 7.90 (3 H, s, CH_3), J ($^{119}Sn-CH_3$) 10 Hz.

E.s.r. Spectroscopy.—Samples contained in Suprasil cells were photolysed in the cavity of a Varian E4 spectrometer with u.v. light from a high pressure mercury arc. The cycloheptatrienyl radical was generated by the photolysis of a solution of di-t-butyl peroxide (*ca.* 50 μl) in cycloheptatriene (*ca.* 100 μl) and toluene (*ca.* 200 μl).

DISCUSSION

The Photolysis of Cyclopentadienylmetallic Compounds.—Table 1 lists the positive (+) and negative (—) results which were obtained when various cyclopentadienylmetallic compounds were photolysed in the e.s.r. cavity, and monitored for the presence of the spectrum of the $C_5H_5\cdot$ radical.

TABLE 1

Photolysis of cyclopentadienylmetallic compounds

C_5H_5M [a]	Solvent [b]	$C_5H_5\cdot$ spectrum
η^5-C_5H_5Li	$MeOCH_2CH_2OMe$ [d]	+
$C_5H_5^-Li^+$ [c]	C_5H_{12} [d]	+
η^3-C_5H_5MgBr	Et_2O [d]	—
$(\eta^3$-$C_5H_5)_2Mg$	C_5H_{12}–Et_2O [d]	—
$(\eta^1$-$C_5H_5)_2Hg$	PhMe [e]	+
$(C_5H_5)_3B$ [g]	Et_2O [d]	—
$C_5H_5\overline{BOC_2H_4O}$ [g]	Et_2O [d]	—
η^1-$C_5H_5SiMe_3$	C_3H_6 [f]	—
$(\eta^1$-$C_5H_5)_nSnR_{4-n}$ [h,i]	C_3H_6 [f]	+
$(\eta^1$-$C_5H_5)_nSnCl_{4-n}$	C_3H_6 [f]	+
$(\eta^5$-$C_5H_5)_2Sn$ (II)	PhMe [f]	+
$(\eta^5$-$C_5H_5)_2TiCl_2$	PhMe [d]	—

[a] All the η^1-compounds are fluxional. [b] C_3H_6 = cyclopropane. [c] In the presence of 18-crown-6. [d] +10 to −40 °C. [e] +10 to −90 °C. [f] +10 to −120 °C. [g] The C_5H_5B compounds are bonded through sp^2 hybridised carbon. [h] R = methyl or butyl, n = 1, 2, or 4. [i] n = 1, 2, or 3.

The spectrum of the $C_5H_5\cdot$ radical which was observed when cyclopentadienyl-lithium was photolysed was rather weak, whereas the derivatives of tin and of mercury showed strong spectra. The derivatives of these latter two metals were therefore investigated in more detail.

Photolysis of all the unsubstituted cylopentadienyltin(IV) compounds, $C_5H_5SnMe_3$, $C_5H_5SnBu_3$, $(C_5H_5)_2SnBu_2$, $C_5H_5SnCl_3$, $(C_5H_5)_2SnCl_2$, $(C_5H_5)_3SnCl$, and $(C_5H_5)_4Sn$ in toluene showed strong spectra of the $C_5H_5\cdot$ radical.

The spectra of any tin-centred radicals would be obscured by that of the cyclopentadienyl radical, but at high microwave power, the spectra of alkyl radicals are saturated, whereas those of tin radicals are not. Our attempts to observe the spectra of the tin radicals directly under high power were frustrated because the cyclopentadienyl radical is anomalous in that its spectrum cannot readily be saturated under these conditions.[25]

However, these systems showed reactions typical of tin-centred radicals, particularly the addition to 1,2-diones, and, for the trialkyltin radicals, the addition to alkenes and the abstraction of bromine from alkyl bromides.[7]

We believe therefore, that photolysis involves simple cleavage of the cyclopentadienyl–tin bond [equation (2)]; this is in contrast to the complications which appear to be associated with the cleavage of the alkyl–metal bond in the derivatives of transition metals described above.*

$$C_5H_5SnX_3 \xrightarrow{h\nu} C_5H_5\cdot + \cdot SnX_3 \qquad (2)$$

(X = alkyl, cyclopentadienyl, or chloride)

Photolysis of di(η^5-cyclopentadienyl)tin(II) similarly showed the spectrum of the cyclopentadienyl radical, but the spectrum was weaker because the reactant has a low solubility in non-polar solvents, and a yellow solid separated during the photolysis. No ethyl radical could be detected when ethyl bromide was added, and we could obtain no direct evidence for the presence of an Sn^I radical. We conclude that photolysis again cleaves the C_5H_5–Sn bond, but the fate of the $C_5H_5\dot{S}\text{n}\!:$ fragment is uncertain [equation (3)]. It is possible that the precipitate is in part a tetramer, $(RSn)_4$, of the type which has been obtained by Sawyer from the decomposition of alkyltin trihydrides.[26]

$$(C_5H_5)_2Sn^{II} \xrightarrow{h\nu} C_5H_5\cdot + [C_5H_5\dot{S}\text{n}\!:] \qquad (3)$$

This photolysis of dicyclopentadienyltin(II) is parallel to that of the σ-bonded compound $[(Me_3Si)_2CH]_2Sn^{II}$, but there the spectrum of the radical $(Me_3Si)_2CH\cdot$ is not observed, presumably because it is rapidly trapped by the tin(II) compound, to give the very persistent radical $[(Me_3Si)_2CH]_3Sn\cdot$.[27] Again, the fate of the tin(I) fragment is not known.

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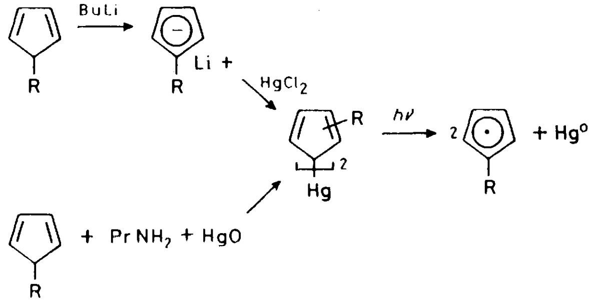
* Photolysis of dicyclopentadienyltitanium dichloride in toluene at −76 °C showed a strong singlet with g 2.0130, ΔH_{pp} 0.6 G, and a weak one with g 2.0035, ΔH_{pp} 2.6 G. These two signals showed no satellites due to Ti coupling and both persisted when the light was shuttered. No spectrum of the $C_5H_5\cdot$ radical could be observed. These results differ from those reported by Tsai and Brubaker who observed signals with g 1.978 and 1.953 both showing titanium coupling.[6]

In contrast to the ready photolysis of unsubstituted cyclopentadienyltin compounds, only a weak spectrum of the methylcyclopentadienyl radical could be observed when tributyl(methylcyclopentadienyl)tin was irradiated However, the cyclopentadienylmercury compounds can readily be prepared by the reactions illustrated in equation (4) and these compounds are photolysed to show good spectra of the corresponding substituted cyclopentadienyl radicals which are thereby rendered accessible for study for the first time: cyclopentadiene and the substituted cyclopentadienes react with radicals such as $Bu^tO\cdot$, $Me_3SiO\cdot$, and $BuS\cdot$ by addition to the diene system as much as by abstraction of hydrogen, and even at high power which saturates the spectra of these adduct radicals, satisfactory spectra of the substituted cyclopentadienyl radicals cannot be obtained.

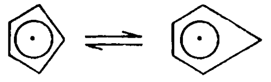


(4)

By the process outlined in equation (4), the e.s.r. spectra of the methyl-, ethyl-, isopropyl-, and t-butylcyclopentadienyl radicals have been obtained.

Two factors which obviously contribute to the photosensitivity of these cyclopentadienylmetallic compounds are that they absorb strongly in the u.v. region of the spectrum (the tin compounds being light yellow), and that the cyclopentadienyl radicals possess 60—80 kJ mol^{-1} stabilisation energy[28] so that the Sn–C_5H_5 bond dissociation energy is probably only 190—210 kJ mol^{-1}.

The Cyclopentadienyl Radical.—The $C_5H_5\cdot$ radical is orbitally degenerate in its most symmetric (D_{5h}) structure (see below), and should undergo Jahn–Teller distortion to a less symmetric (C_{2v}) configuration. The vibrational barrier for isomerisation by equation (5) is calculated to be very small (4—113 J mol^{-1}),[29] and the molecule would be expected to oscillate between the five pairs of C_{2v} forms.


(5)

The e.s.r. spectrum of the radical above 70 K shows that all five hydrogen atoms are effectively equivalent, which would be compatible with rapid equilibration between the various distorted structures. However, in a matrix of a single crystal of cyclopentadiene below 70 K,[30] or in a neon matrix below 4 K,[31] the radical shows a more complex spectrum which has been ascribed to the Jahn–Teller distorted, C_{2v}, structure, stabilised by the matrix.

Our spectrum of the cyclopentadienyl radical (Figure 1) showed that a(5 H) varied linearly with temperature from 5.965 G at −20 °C to 6.005 G at −90 °C, whence $da(H)/dT = -0.57$ mG K^{-1}, and Q in the McConnell equation $a(H_\alpha) = Q\rho_{C\alpha}$ varies from 29.83 G at −20 °C to 30.03 G at −90 °C, close to the values which have been reported previously.

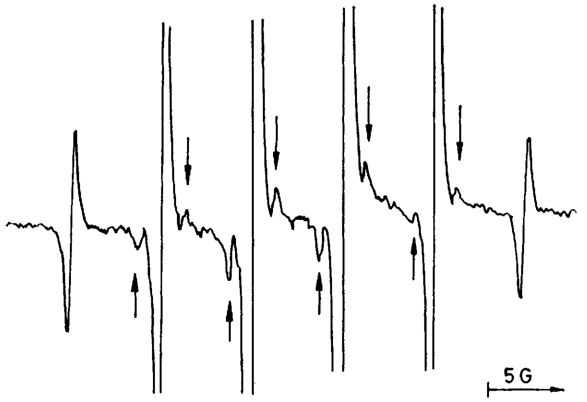
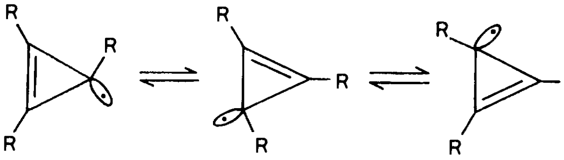


FIGURE 1 E.s.r. spectrum of the cyclopentadienyl radical obtained from the photolysis of cyclopentadienyltin trichloride in toluene at −37 °C, showing (arrowed) ^{13}C satellites

The magnitude of the ^{13}C hyperfine coupling, 2.6 G, is in reasonable agreement with the value of +1.6 G calculated from the Karplus–Fraenkel[32] equation for a π-radical of D_{5h} symmetry. A similar measure of agreement is found between the experimental (2.2 G) and calculated (+1.1 G) values for $a(^{13}C)$ in the cycloheptatrienyl radical.[33] In contrast, the tri-t-butylcyclopropenyl radical shows $a(^{13}C) = 30.0$ G, against a calculated value of 2.6 G, showing that it is not a π-radical but an equilibrating set of σ-radicals [equation (6)].[34]



(6)

Our spectrum of the cyclopentadienyl radical establishes that any distortion away from five-fold symmetry must retain the plane of symmetry, and that the $C_5H_5\cdot$ radical has none of the σ-character exhibited by $C_3Bu^t_3\cdot$.

The resistance to power saturation referred to above, has been observed previously for the cyclopentadienyl radical in an adamantane matrix (where it can be exploited to enhance the spectrum of the $C_5H_5\cdot$ radical compared with the spectra of other radicals),[25,35] and also for other highly symmetric radicals such as $C_6H_6^{\cdot-}$,[36] $C_6H_6^{\cdot+}$,[37] $C_6(CF_3)_6^{\cdot-}$,[38] $C_7H_7\cdot$,[36,39] $C_8H_8^{\cdot-}$,[39] and coronene$^{\cdot+}$.[40] This effect has been ascribed to the reduction of spin–lattice relaxation times either by the dynamic Jahn–Teller effect discussed above,[38,41] or by spin–orbit interaction associated with the electronic orbital motion round the aromatic ring. The fact that the resistance to saturation appears to be similar in the cyclopentadienyl radical, which is orbitally degenerate, and in the methylcyclopentadienyl radical, in which the substituent breaks the orbital degeneracy (see below), appears to suggest that the ring current effect makes a substantial contribution.

An unexpected feature which we found with the e.s.r. spectrum of the cyclopentadienyl radical was that its lines are broadened in the presence of an organic bromide or iodide. This effect is observed both in the absence or the presence of the generation of the organic radical from the organic halide.

Photolysis of $C_5H_5SnMe_3$, $C_5H_5SnBu_3$, or $(C_5H_5)_2SnBu_2$ in the presence of a variety of alkyl bromides, R'Br (*e.g.* R′ = Et, Pr^i, or Bu^t) or acyl bromides[42] (*e.g.* R′ = cyclopropylacyl or cyclobutylacyl) showed strong, sharp spectra of the appropriate radical R′•, presumably formed by reaction (7), but the lines of the cyclopentadienyl radical were broadened to a degree depending on the concentration of the organic bromide. A typical spectrum is illustrated in ref. 7.

$$C_5H_5SnR_3 \longrightarrow C_5H_5\cdot + R_3Sn\cdot \xrightarrow{R'Br} R'\cdot + R_3SnBr \quad (7)$$

This effect is useful in that it provides a convenient method of observing the spectrum of various radicals R•′ in the absence of any superimposed spectrum of $C_5H_5\cdot$.

The spectrum of the $C_5H_5\cdot$ radical obtained from the photolysis of $(C_5H_5)_2Hg$ shows the same line-broadening effect in the presence of bromides R'Br, but now no R′• radical is formed by abstraction of bromine. A typical series of spectra of the $C_5H_5\cdot$ radical which are observed when increasing amounts of ethyl bromide are added, are shown in Figure 2.

Photolysis of the organotin compounds in the presence of alkyl iodides, R'I, similarly shows the spectrum of the radical R′•, and the broadened spectrum of the cyclopentadienyl radical, but alkyl chlorides, R'Cl (R′ = Pr^i, Bu^t, or CH_3COCH_2) are without effect. When carbon tetrachloride is added, the sharp $C_5H_5\cdot$ spectrum is superimposed on that of an allylic radical, *a* (4 H) 15.0, *a* (1 H) 2.6, *a* (^{117}Sn) 106.4, and *a* (^{119}Sn) 111.0 G, which is presumably the adduct (1).* The same spectrum of (1) is observed when bromotrichloromethane is added instead, but now the spectrum of the cyclopentadienyl radical is broadened beyond recognition.

The cycloheptatrienyl radical is equally sensitive to line broadening by added alkyl bromides. Figure 3 shows a series of spectra of the $C_7H_7\cdot$ radical obtained by the photolysis of di-t-butyl peroxide in the presence of cycloheptatriene and increasing amounts of added ethyl bromide.

As far as we are aware, this line-broadening effect has not been reported previously. We tentatively suggest that the annulene radical and the bromide or iodide form a charge-transfer complex in which the signals are broadened by interactions involving the magnetic and nuclear quadrupole moments of the halides.

The Hückel Molecular Orbital (*HMO*) *Model for Substituted Cyclopentadienyl Radicals.*—The e.s.r. spectra of the substituted cyclopentadienyl radicals can be interpreted in terms of the perturbation of the degenerate highest occupied molecular orbitals, following the procedure which has been most successful for the benzene radical anions[43] and cations,[44] the cycloheptatrienyl radicals,[45] and the cyclo-octatetraene[46] radical anions. Sakurai *et al.*[47] have already analysed the spectra of some silyl-substituted cyclopentadienyl radicals in these terms, but they were unable to study the alkyl-substituted analogues because no general method for generating them was available.

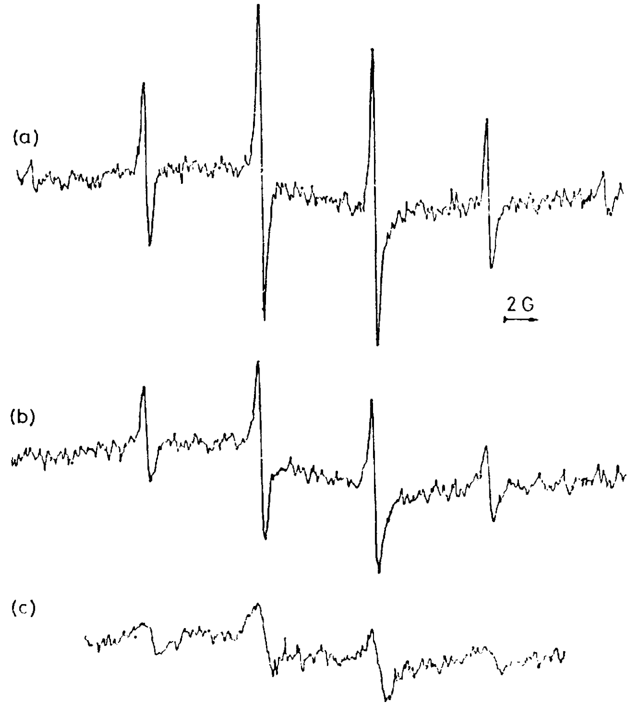
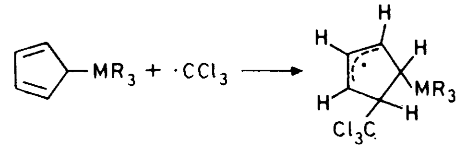


FIGURE 2 Broadening of the lines of the e.s.r. spectrum of the cyclopentadienyl radical during the photolysis of bis(cyclopentadienyl)mercury in toluene (250 µl) containing (a) 0 µl, (b) 10 µl, and (c) 15 µl of ethyl bromide at −60 °C



(8)

(1)

The HMO energy diagram for the cyclopentadienyl radical is illustrated in Figure 4. The degenerate levels ψ_A and ψ_S will be equally populated, resulting in a radical of D_{5h} symmetry as discussed above.

$$\psi_S = 0.632\phi + 0.195(\phi_2 + \phi_3) - 0.512(\phi_3 + \phi_4) \quad (9)$$

$$\psi_S = 0.602(\phi_2 - \phi_5) + 0.372(\phi_3 - \phi_4) \quad (10)$$

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* Photolysis of bromotrichloromethane in the presence of cyclopentadienyltrimethylsilane shows a very similar spectrum of (1; MR_3 = $SiMe_3$), *a* (2H) 13.7, *a* (1H) 16.0, *a*(1H) 18.2, and *a* (1H) 2.6 G.

Introduction of an electron-repelling substituent at C(1) will not affect the energy of ψ_A which has a nodal plane through this position, but ψ_S, with a high electron density (0.632^2) at C(1) will be destabilised as shown in Figure 5. Conversely, an electron-attracting substituent will again leave ψ_A unaffected, but will stabilise ψ_S.

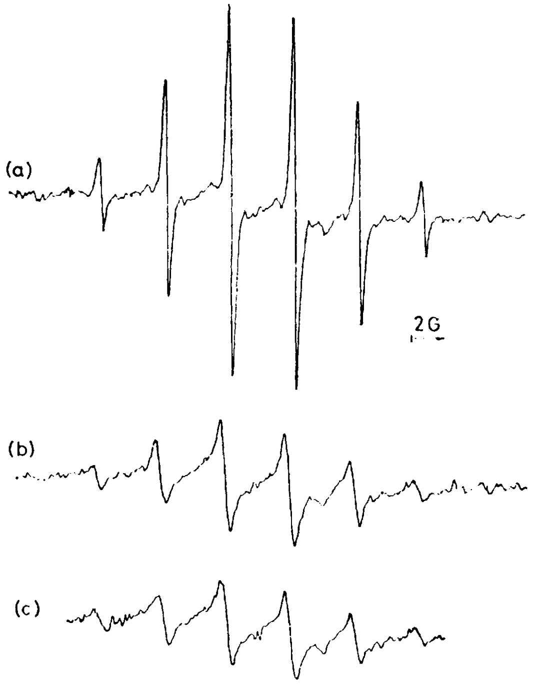


FIGURE 3 Broadening of the lines of the e.s.r. spectrum of the cycloheptatrienyl radical during the photolysis of di-t-butyl peroxide (100 μl) in the presence of cycloheptatriene (100 μl) in cyclopentane (400 μl) containing (a) 0 μl, (b) 10 μl, and (c) 15 μl of ethyl bromide at −60 °C

If the resulting energy separation, ΔE, is large, the unpaired electron will occupy exclusively the higher of the two energy levels, and the radical will have the configuration $\psi_A^2\psi_S^1$ or $\psi_S^2\psi_A^1$ as appropriate. The hyperfine coupling constants at position i will then be related to the McConnell Q value for the cyclopentadienyl radical by equation (11) where c_i is the coefficient at the

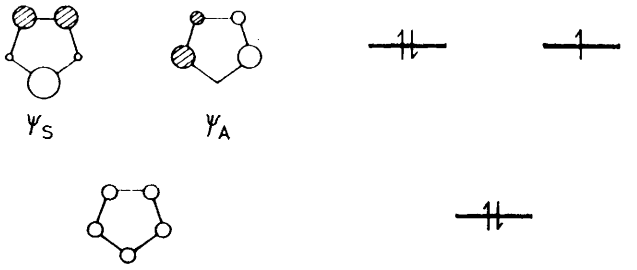


FIGURE 4 HMO diagram for the cyclopentadienyl radical

$$a_i = c_i^2 Q \qquad (11)$$

ith carbon atom in ψ_S or ψ_A, respectively. Values of a_i calculated from equation (11) are given in Table 2.

For a substituted cyclopentadienyl radical, use is made of a parameter a_1^*, which is the imaginary proton splitting corresponding to the spin density at the substituted position C(1), and is defined by equation (12).

$$a_1^* = Q - \sum_{2-5} a_i \qquad (12)$$

If the energy separation, ΔE, between ψ_A and ψ_S is small, thermal mixing will occur between the configurations $\psi_A^2\psi_A^1$, and the observed value of a_i will be the average of the extreme values, a_{iA} and a_{iS}, weighted by the probabilities, P_A and P_S, that the unpaired electron occupies the ψ_A and ψ_S MO respectively [equation (13)].

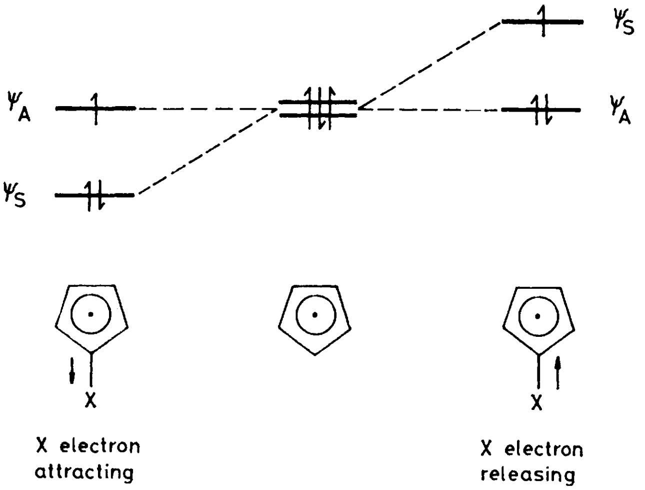


FIGURE 5 Splitting of degenerate ψ_S and ψ_A MOs by electron-attracting and electron-releasing substituents

$$a_i = P_A a_{iA} + P_S a_{iS} \qquad (13)$$

The energy separation between ψ_A and ψ_S can then be derived from the temperature dependence of P_A and P_S.

$$P_A/P_S = \exp(\Delta ERT) \qquad (14)$$

Alkylcyclopentadienyl Radicals.—Values for the observed proton hyperfine coupling constants for the methyl-, ethyl-, isopropyl-, and t-butyl-cyclopentadienyl radicals are given in Table 3, and typical spectra are illustrated in Figures 6 and 7. The correlation with the calculated values for the $\psi_A^2\psi_S^1$ configuration, given in Table 2, are very satisfactory in view of the severe approximations involved in Hückel theory. We conclude that, at −70 °C, the configuration of these alkylcyclopentadienyl radicals is essentially pure $\psi_A^2\psi_S^1$, the alkyl substituents breaking the orbital degeneracy by electron repulsion, as they do in the [6]-, [7]-, and [8]-annulene radicals which have been studied previously.

TABLE 2

Calculated hyperfine coupling constants for $\psi_A^2\psi_S^1$ and $\psi_S^2\psi_A^1$ cyclopentadienyl radicals at −70 °C

Configuration	Hyperfine coupling constants (G) [a]		
	$a(H_1)$	$a(H_{2,5})$	$a(H_{3,4})$
$\psi_A^2\psi_S^1$	11.97	1.14	7.86
$\psi_S^2\psi_A^1$	0.00	10.86	4.15

[a] Calculated from equation (11), taking Q (−70 °C) = 29.97 G.

The hyperfine coupling constants for the ring protons in the methyl-, isopropyl-, and t-butyl-cyclopentadienyl radicals were independent of temperature within the experimental error over the range −40 to −70 °C, but the values for the ethylcyclopentadienyl radical varied with temperature as shown in Table 4. The trend in the values of $a(H_{2,5})$ and $a(H_{3,4})$ would be compatible with the mixing in of some of the $\psi_S{}^2\psi_A{}^1$ configuration at the higher temperatures, but $a^*(H_1)$ increases with temperature whereas on this picture it should fall, and the effect may instead by connected with the hyperconjugative interaction between the alkyl group and the π-electron system as discussed below.

TABLE 3

Observed hyperfine coupling constants for alkylcyclopentadienyl radicals at −70 °C

Radical	Hyperfine coupling constants (G) [a]				
	$a^*(H_1)$	$a(H_{2.5})$	$a(H_{3.4})$	$a(H_\beta)$	a(Me)
$CH_3C_5H_4\cdot$	12.69	0.90	7.75	15.30 [b]	
$MeCH_2C_6H_4\cdot$	12.15	0.94	7.98	15.82 [c]	
$Me_2CHC_5H_4\cdot$	12.47	1.17	7.59	12.49 [d]	0.42
$Me_3CC_5H_4\cdot$	12.07	1.40	7.55		0.65

[a] Errors are ±0.01 G except for $MeC_5H_4\cdot$ where they are ±0.05 G. [b] From −70 to 0 °C, $da/dT = -5.7$ mg K^{-1}. [c] From −70 to −40 °C, $da/dT = -17.8$ mG K^{-1}. [d] From −70 to −50 °C, $da/dT = -6.25$ mG K^{-1}.

TABLE 4

Temperature dependence of the hyperfine coupling constants in the ethylcyclopentadienyl radical

T/°C	$a^*(H_1)$	$a(H_{2,5})$	$a(H_{3,4})$
−39	12.85	1.02	7.50
−47	12.71	1.00	7.60
−56	12.47	0.98	7.75
−70	12.13	0.94	7.98

If the magnitude of the hyperfine coupling constant of the CH_3 group in $CH_3C_5H_4\cdot$ were dependent only on the spin density at C(1), it should be given by equation (15).

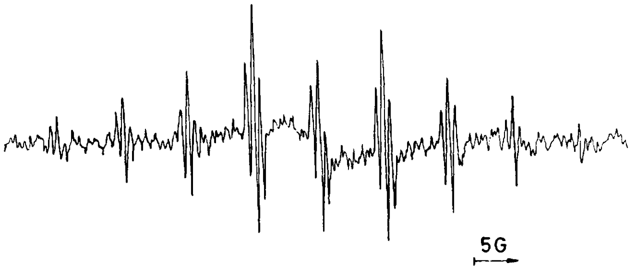


FIGURE 6 E.s.r. spectrum of the methylcyclopentadienyl radical, obtained by the photolysis of bis(methylcyclopentadienyl)mercury in toluene at −60 °C

If $A = 1$ G, $B = 58$ G, $\langle\cos\rangle^2\theta = 1/2$, and $\rho = 0.632^2$, a(CH) is calculated to be 12.0 G. Alternatively, the value of a^* [H(1)] in $CH_3C_5H_4\cdot$ may be taken to imply that $\rho_{C\alpha} = 12.69Q$ when equation (15) gives

$$a(H_\beta) = \rho_{C\alpha}(A + B\cos^2\theta) \qquad (15)$$

$a(CH_3) = 12.7$ G. Both values are substantially less than the observed value of 15.30 G. This discrepancy is commonly observed in methylannulene radicals, and it has been ascribed to hyperconjugative interaction between the π-system of the ring and the methyl group, which will depend on both the value of $\rho_{C\alpha}$ and the proximity of the two energy levels which are involved.[48]

The higher value of $a(2H_\beta)$ in the ethylcyclopentadienyl radical, and its negative temperature coefficient, suggest that this radical is most stable in the staggered conformation (2), like the n-propyl radical,[49,50] and this is supported by the fact that, in this conformation the C–H bonds of the methyl group cannot adopt a W conformation with respect to the p-orbital containing the unpaired electron, and $a(CH_3)$ is too small to be measured.

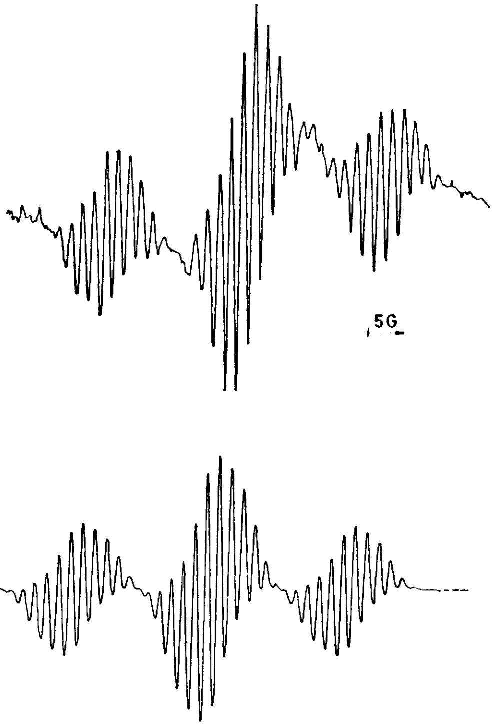
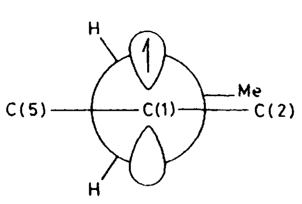


FIGURE 7 (a) E.s.r. spectrum of the t-butylcyclopentadienyl radical obtained by the photolysis of bis-(t-butylcyclopentadienyl)mercury in toluene at −50 °C. (b) Computer simulation, taking $a(H_{2.5})$ 1.40 G, $a(H_{3,4})$ 7.55 G, $a(Bu^t)$ 0.65 G

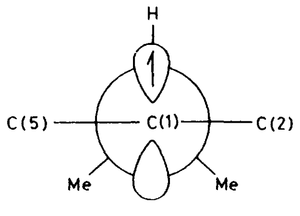
The negative temperature coefficient of $a(H_\beta)$ in the isopropylcyclopentadienyl radical suggests that it prefers the eclipsed conformation (3) at low temperature, like the isobutyl radical; the low value of the hyperfine coupling constant is then out of line with that for the methylcyclopentadienyl or ethylcyclopentadienyl radicals, though in agreement with that predicted by equation (15), and may reflect the reduced hyperconjugating ability of the isopropyl group.

The Deuteriocyclopentadienyl Radical.—The deuterioannulene radicals have attracted a lot of attention since Lawler *et al.*[51] showed that deuterium breaks the orbital degeneracy in $C_6H_5\dot{D}^-$ so that $a(H_{2.3.5.6}) = 3.95$ G, and $a(H_4) = 3.49$ G.[51] Until now, this type of effect has been observed only in [6]annulene radical anions (*e.g.* various deuterium-substituted benzene[52] and naphthalene[53] radical anions), any splitting being within the linewidth in the deuteriobenzene radical cations,[37] the deuteriocycloheptatrienyl radical,[54] and the deuterio-cyclo-octatetraenyl radical anion.[55] The effect is accompanied by anomalous values of the ratio *a*(H) : *a*(D), and of the temperature coefficient of *a*(H).

By photolysis of a 1 : 1 mixture of $Bu_3SnC_5H_5$ and $Bu_3SnC_5H_4D$, we obtained the superimposed spectra of the radicals C_5H_5· and C_5H_4D· as shown in Figure 8.



(2)



(3)

The ratio *a*(H, C_5H_5) : *a*(D, C_5H_4D·) is 6.74, much larger than the value of 6.514 calculated from the magnetogyric ratios of the two nuclei.* This implies that the deuterium is attached to a carbon atom with low electron density, that is C(1) in the ψ_A MO (Figure 2), the C_5H_4D· radical having predominantly the configuration $\psi_S{}^2\psi_A{}^1$.

This should render $a(H_{2,5})$ and $a(H_{3,4})$ non-equivalent, resulting in further splitting of the central three triplets in the spectrum (see Figure 8, inset). The expanded spectrum in Figure 8 illustrates this splitting into triplets and doublets respectively for the third and fourth groups of triplets, from which the hyperfine coupling constants were obtained by computer simulation of the spectra. The results are given in Table 5, and are best fitted by taking P_A 0.515 and P_S 0.485 [equation (11)], that is the C_5H_4D· radical has the configuration $\psi_S{}^{1.515}$ $\psi_A{}^{1.485}$, and the ψ_A is 100 J mol^{-1} higher in energy than the ψ_S MO.

TABLE 5

Observed and calculated hyperfine coupling constants for the C_5H_4D· radical

	Hyperfine coupling constant (G)		
	$a(H_{2,5})$	$a(H_{3,4})$	$a(D)$
Observed [a]	6.14	5.92	0.89
Calc. for $\psi_S{}^{1.5}\psi_A{}^{1.5}$	6.00	6.00	0.92 [b]
Calc. for $\psi_S{}^{1.515}\psi_A{}^{1.485}$	6.15	5.95	0.89 [b]

[a] At −75 °C in toluene. [b] Calculated from $(Q-\sum_{2-5}a_i)/6.514$.

Two principal models have been proposed to account for the perturbation of the annulene MOs by a deuterium substituent.[52,53,58] The first takes account of the fact that deuterium releases electrons more readily than hydrogen, which will perturb the Coulomb integral (α). This would tend to place the unpaired electron in the C_5H_4D· radical principally in the ψ_S MO.

The second model considers the effect which out-of-plane vibration of hydrogen or deuterium has on the resonance integral (β). This vibration will be followed by a rocking motion of the *p*–π orbital on the proximate carbon atom, which will reduce the degree with which it overlaps with the corresponding *p*–π orbitals on the two adjacent carbon atoms. This motion will be destabilising, without effect, or stabilising depending on whether the MO is bonding, non-bonding, or antibonding between the particular atoms involved, and any such effect will be smaller when hydrogen is replaced by deuterium, because the amplitude of vibration will be reduced. On this model the introduction of a deuterium atom into C_5H_5· will stabilise ψ_S because it is bonding between C(1) and C(2), and between C(1) and C(5), but ψ_A, with a node at C(1), will not be effected (Figure 2); the radical should, therefore, prefer the configuration $\psi_S{}^2\psi_A{}^1$.

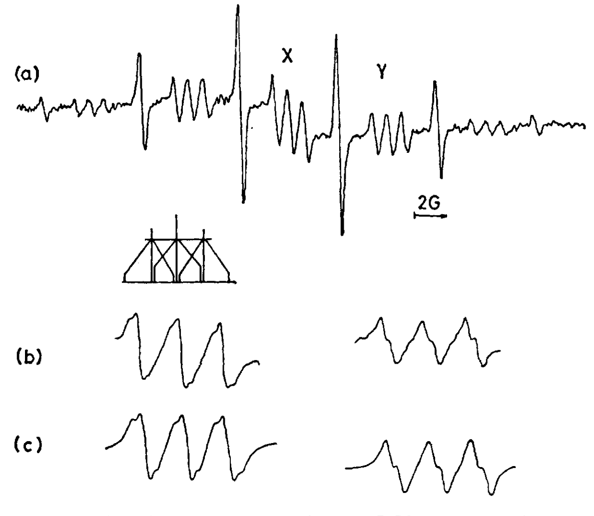


FIGURE 8 (a) E.s.r. spectra of the C_5H_5· radical (sextet of singlets) and C_5H_4D· radical (quintet of triplets) obtained from the photolysis of a 1 : 1 mixture of $C_5H_5SnBu_3$ and $C_5H_4DSnBu_3$ in toluene at −40 °C. Inset: stick diagram of the further splitting of each line of the second, third and fourth triplets if $a(H_{2,5}) \neq a(H_{3,4})$. (b) Expension of the triplets X and Y showing further resolution into triplets and doublets, respectively. (c) Computer simulation of the triplets X and Y, taking $a(H_{2,5})$ = 6.14 G, $a(H_{3,4})$ = 5.92 G, and *a*(D) 0.89 G

Our results are therefore uniquely consistent with the vibrational perturbation of the resonance integral β being of predominant importance. The same unambiguous choice between the two models for perturbation could be made for the [1,4,5,8-$^2H_4$]- and [2,3,6,7-$^2H_4$]-naphthalene radical anions,[53] but in the deuteriobenzene radical anions,[52,58] perturbation of the Coulomb integral and of the resonance integral operate in the same sense, and the choice in favour of the β-perturbation had to be based less securely on the magnitude of the effect.

The energy shift for the ψ_A MO should be given by

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* In a π-radical, *a*(H) : *a*(D) is usually *less* than 6.514 because out-of-plane vibration of hydrogen reduces the splitting from spin-polarization from the proximate carbon, and introduces a small hyperconjugative contribution to the coupling, usually with the opposite sign, from the adjacent carbon atoms. The vibrational amplitude of C–H is greater than that of C–D, and *a*(H) is reduced disproportionately. As the temperature increases, the vibrational amplitude increases, hence d*a*(H)/d*T* in a π-radical is usually negative. The only previous π-radicals that we are aware of which have *a*(H) : *a*(D) > 6.514 [and a positive temperature coefficient of *a*(H)] are the [1-^{2}H]phenalenyl radical [*a*(H) : *a*(D) = 6.54 ± 0.01] [56] and the [1,4-$^2H_2$]-2,3,5,6-tetramethoxybenzene radical cation [*a*(H) : *a*(D) = 6.61 ± 0.05],[57] in both of which the hyperfine coupling by spin polarisation from the proximate carbon atom and by hyperconjugation from the adjacent carbon atoms have the same sign.

equation (16),[52,58] where δ is the change in β when hydrogen is replaced by deuterium. For a series of deuteriobenzenes, the best fit with the experimental data was obtained by taking $\delta = 0.002\ \beta$, where $\beta = 167$ kJ mol^{-1}. If this value of δ is accepted for the $C_5H_4D\cdot$ radical, equation (16) gives ΔE *ca.* 165 J mol^{-1}, near to the value of 100 J mol^{-1} which is observed.

$$\Delta E \simeq 2c_i(\delta_{i,i+1}c_{i+1} + \delta_{i,i-1}c_{i-1}) \qquad (16)$$

Conclusions.—The cyclopentadienyl radical is the simplest annulene π-radical which has been prepared. Its electrical neutrality avoids some of the complications which may arise in the interpretation of results with the [6]annulene anions and cations, and the small size of the ring, with the associated large values of the atomic coefficients, makes it very sensitive to the effect of substituents. The cyclopentadienylmetallic compounds are convenient precursors of a wide variety of substituted cyclopentadienyl radicals and this system is probably the best yet available for investigating the interaction of substituents with a π-electron system.

In correspondence with Professor Sakuri, we have learned that he has independently carried out a similar investigation to ours, in which the substituted cyclopentadienyl radicals have been generated by a rather different technique from that which we have used.[59] The effects of deuterium and alkyl substituents which he and his colleagues have observed are broadly in agreement with the results reported here.

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