An Electron Spin Resonance Study of Cyclopentadiene Radical Cations

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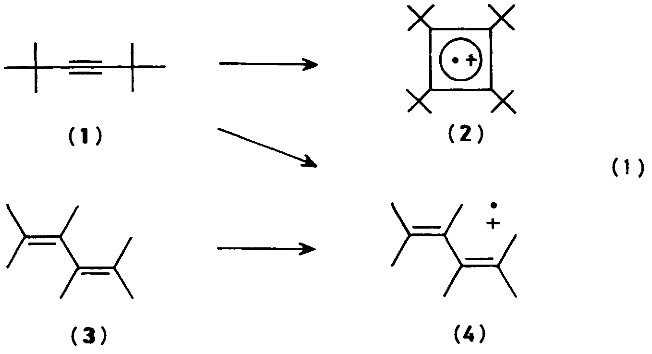
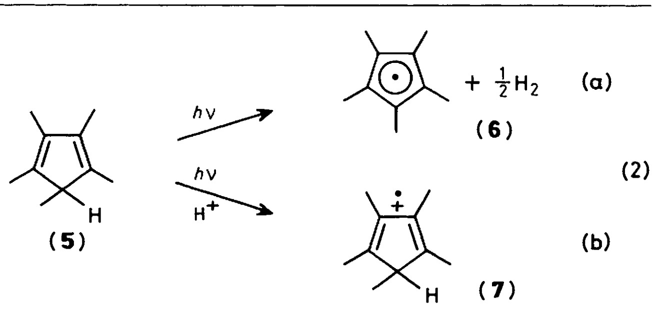
If solutions of hexa-, penta-, tetra-, or tri-alkylcyclopentadienes in trifluoroacetic acid are irradiated with u.v. light, the e.s.r. spectra of the corresponding alkylcyclopentadiene radical cations can be observed. The radical cation $Me_5C_5H^{+\bullet}$ can also be obtained from decamethylbi(cyclopentadienyl), Me_5C_5–C_5Me_5, under similar conditions. The spectra of $Me_6C_5^{+\bullet}$, $Me_5C_5H^{+\bullet}$, and $Me_4C_5H_2^{+\bullet}$ can be analysed in terms of single isomers. The sp^3 carbon atom of the ring lies in the nodal plane of the SOMO, and substituents at this position show only small hyperfine coupling constants. The radical cation $Me_5C_5H^{+\bullet}$ shows no evidence of fluxionality on the e.s.r. timescale up to 328 K. The spectra of $Me_4EtC_5H^{+\bullet}$, $Me_3Et_2C_5H^{+\bullet}$, and $Me_3C_5H_3^{+\bullet}$ apparently relate to mixtures of prototropic isomers. Experiments with optical cut-off filters show that the primary photochemical process involves excitation of the protonated diene.

Most of the hydrocarbon radical cations which have been characterised in liquid solution are derived from extended π-systems; little work has been reported on simple 1,3-dienes.[1] Since 1981, the cyclobutadiene radical cations [*e.g.* (**2**)] have been systematically studied,[2] but at the time the present work was initiated, no other type of diene radical cation had been identified.

We were encouraged to look for such species by our chance observation of the spectrum of the hexamethylbutadiene radical cation. If a solution of di-t-butylacetylene (**1**) in dichloromethane containing aluminium chloride is irradiated at about 210 K, the e.s.r. spectrum of the tetra-t-butylcyclobutadiene radical cation (**2**) can be observed [equation (1)].[3] However, before the solution was irradiated a different spectrum could frequently be detected. This could be simulated as a septet of septets of septets. The hyperfine coupling constants are close to those which would be predicted for the permethylated butadiene radical cation (**4**); indeed the same spectrum was obtained from hexamethylbutadiene itself (**3**).[4]



A promising field in which to look for further examples of 1,3-diene radical cations appeared to be that of the alkylated cyclopentadienes which we already had available. We had shown that pentamethylcyclopentadiene (**5**) is remarkably photosensitive, and that if it is irradiated with u.v. light in a hydrocarbon solvent, hydrogen gas is evolved, and the spectrum of the pentamethylcyclopentadienyl radical (**6**) can be observed [equation (2)].[5]



On the principle that a radical cation can often be regarded as the conjugate acid of a neutral radical [equation (3)], we

$$R^\bullet + H^+ \rightleftharpoons RH^{+\bullet} \qquad (3)$$

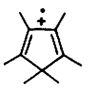
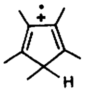
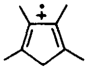
reasoned that, without prejudice as to the mechanism of the process, photolysis of pentamethylcyclopentadiene in the presence of an acid might lead to the formation of the cyclopentadiene radical cation (**7**).[6] We report here the results of such experiments with various alkylated cyclopentadienes.

Results

E.s.r. Spectra.—1,2,3,4,5-Pentamethylcyclopentadiene, freshly purified by g.l.c., dissolved in trifluoroacetic acid to give a deep red solution. Sometimes such solutions, prior to irradiation, showed a weak e.s.r. spectrum; this may have been caused by laboratory light, or by adventitious oxygen. When the solution was irradiated at 163 K with light from a high-pressure mercury arc unfiltered or passed through filters to cut off wavelengths < 390 nm, the intensity of the spectrum was greatly enhanced as shown in Figure 1(a). This could be simulated [Figure 1(b)] using the hyperfine coupling constants given in Table 1; the spectral parameters were unchanged over the range 258—328 K, although at the higher temperatures the spectrum was much weaker. No evolution of gas was apparent.

We have previously shown that the spectrum of the pentamethylcyclopentadienyl radical can also be observed when decamethylbi(cyclopentadienyl) (**8**) is irradiated in an inert solvent. If trifluoroacetic acid is used as the solvent, the same spectrum as that shown in Figure 1 is again observed. We

Table 1. E.s.r. spectra of cyclopentadiene radical cations

			Hyperfine coupline constants (G)			
	Solvent	*T*/K	1,4	2,3	5	*g*
	CF_3CO_2H	263	14.4(6H)	4.0(6H)	1.3(6H)	2.0024
	CF_3CO_2H	259	15.0(6H)	4.0(6H)	0.8(3H) 1.6(1H)	2.0027
	CF_3CO_2H	263	15.2(6H)	4.0(6H)	1.4(2H)	2.0022
	Cl_3CF		11.6(2H)	3.5(2H)	<2	*a*

[a] T. Shida, Y. Egawa, H. Kato, and H. Kubodera, *J. Chem. Phys.*, 1980, **73**, 5963. The reported linewidth was 3.2 G.

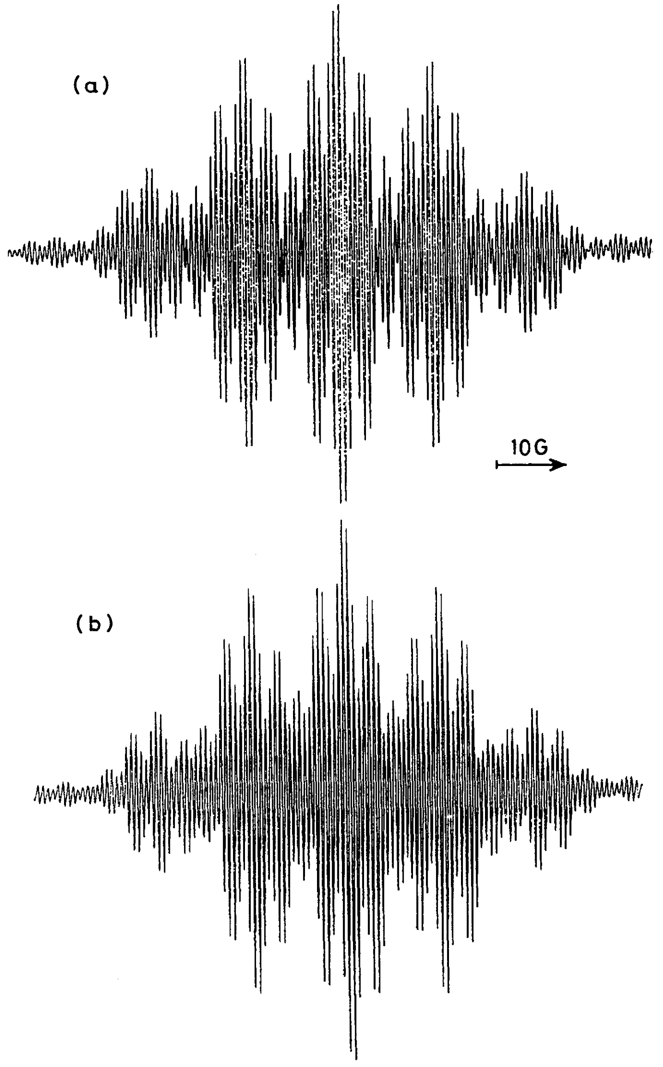


Figure 1. (a) Observed and (b) simulated e.s.r. spectra of $Me_5C_5H^{+\bullet}$ (**7**) in CF_3CO_2H at 259 K

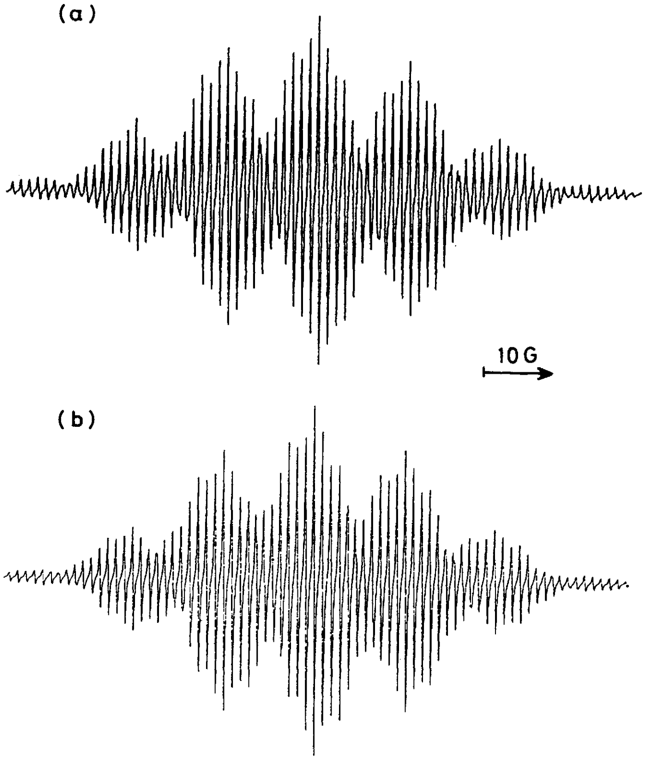
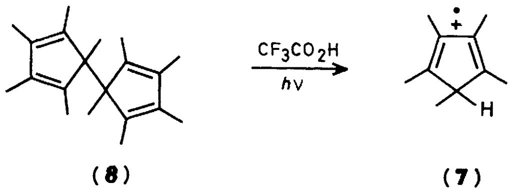


Figure 2. (a) Observed and (b) simulated e.s.r. spectra of $Me_6C_5^{+\bullet}$ (**10**) in CF_3CO_2H at 263 K

assign this spectrum to the pentamethylcyclopentadiene radical cation (**7**) [equations (2b) and (4)].



(4)

If the light was shuttered at 263 K, the intensity of the spectrum was halved in about 30 s, but the kinetics of the decay were not simple, and the spectrum could still be detected after 2 h.

No spectrum was observed when hexamethylcyclopentadiene (**9**) in cyclopentane was irradiated with u.v. light. In trifluoroacetic acid in the dark, a weak spectrum was observed, which could not be analysed satisfactorily. The presence of this spectrum appeared to be related to the age of the sample (**9**), and we believe that it may signify the presence of a product from atmospheric oxidation. When the solution was irradiated with filtered or unfiltered u.v. light, this spectrum disappeared and was replaced by that shown in Figure 2(a). This can be simulated [Figure 2(b)] using the hyperfine coupling constants given in Table 1, and we assign it to the hexamethylcyclopentadiene radical cation (**10**).

Under similar conditions, 1,2,3,4-tetramethylcyclopentadiene (**11**)[†] gave the spectrum shown in Figure 3(a). This can be

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[†] In compounds (**11**), (**13**), (**15**), (**17**), and (**18**), the numbering is intended to denote only the relative positions of the alkyl substituents; a mixture of prototropic isomers may be present.

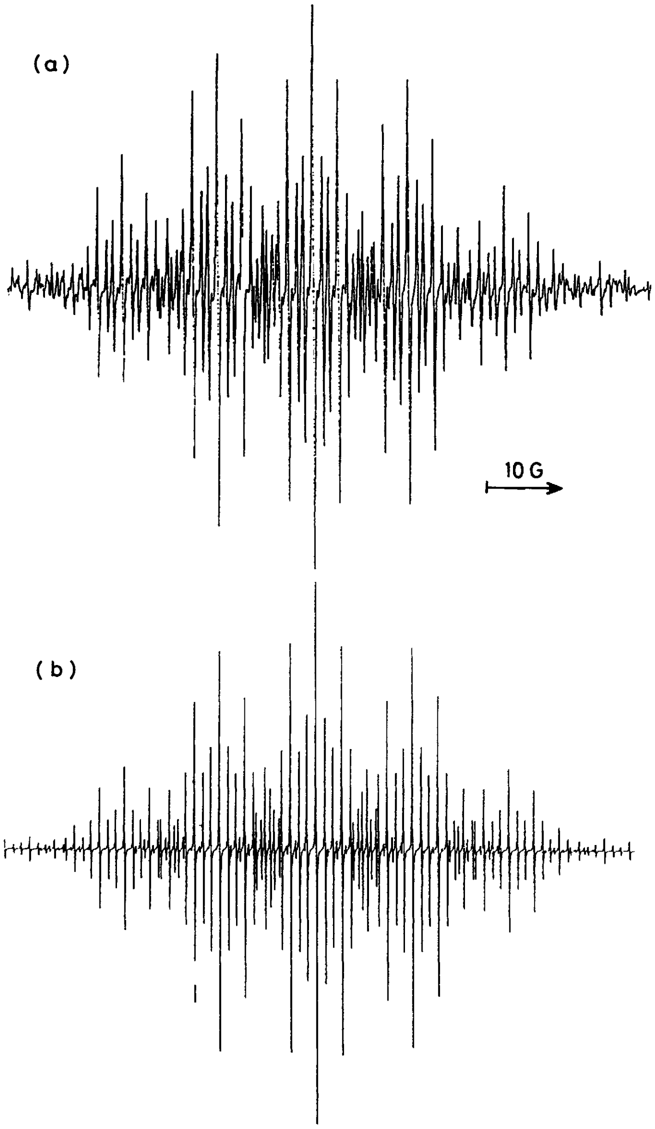
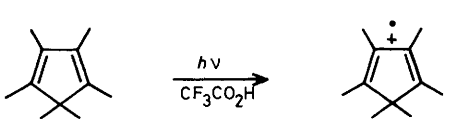


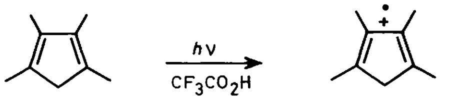
Figure 3. (a) Observed and (b) simulated e.s.r. spectra of $Me_4C_5H_2^{+\bullet}$ (12) in CF_3CO_2H at 263 K



(5)

(9) **(10)**

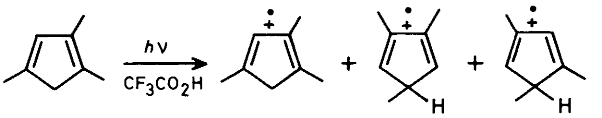
simulated [Figure 3(b)] with the parameters given in Table 1, and we assign it to the corresponding radical cation (**12**).



(6)

(11) **(12)**

1,2,4-Trimethylcyclopentadiene (**13**) gave an orange solution in trifluoroacetic acid, which showed a weak spectrum before photolysis. The intensity of the spectrum was greatly enhanced when the solution was irradiated with u.v. light at 261 K, but we have not been able to simulate it satisfactorily, and we assume that it represents a mixture of the various possible isomers (**14a**—**c**).

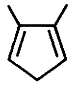


(7)

(13) **(14a)** **(14b)** **(14c)**

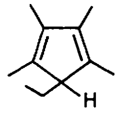
Similarly 2,3-dimethylcyclopentadiene (**15**) and 5,5-dimethylcyclopentadiene (**16**) gave complex spectra which could not be fully analysed. Again, it appears likely that an isomeric mixture of radical cations is present, together perhaps with the radical cation of the dimer resulting from the electron-hole-catalysed Diels–Alder reaction. We have previously identified such a dimeric radical cation which is formed in the one-electron oxidation of 1,4-dimethylcyclohexa-1,3-diene.[7]

No e.s.r spectra were observed from methylcyclopentadiene or from cyclopentadiene itself under similar conditions.



(15)

(16)



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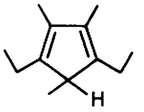


(18)

Similar experiments were carried out with 1,2,3,4-tetramethyl-5-ethylcyclopentadiene (**17**) and 1,4-diethyl-2,3,5-trimethylcyclopentadiene (**18**). Strong spectra were obtained, resembling those of $Me_5C_5H^{+\bullet}$ and $Me_6C_5{}^{+\bullet}$. The magnitudes of some of the hyperfine coupling constants could be obtained, and these, and the overall spectral widths and the *g*-values, were consonant with those expected for the penta-alkylcyclopentadiene radical cation, but the spectra were more complicated than simulations based on the symmetrical structures (**17**) and (**18**). We assume that one-electron oxidation occurs, as with pentamethylcyclopentadiene, but that the products consist of a number of prototropically isomeric radical cations.

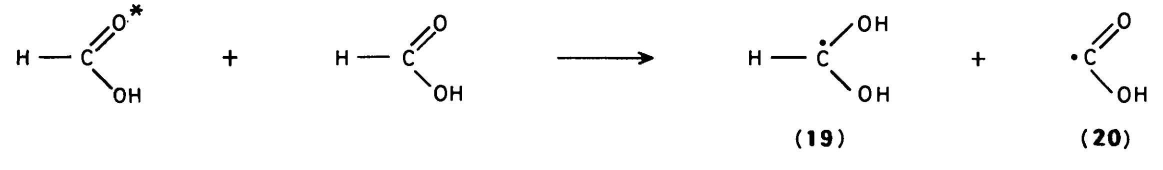
Variation of the Acid.—Experiments were carried out with solutions of pentamethylcyclopentadiene in various acids. With difluoroacetic acid, irradiation at 278 K gave rise to the same spectrum of the $Me_5C_5H^{+\bullet}$ radical cation as was observed with trifluoroacetic acid, and a gas was seen to be evolved. When the light was shuttered, the spectrum decayed to one-third of its initial intensity in 2 min.

When 98% formic acid alone was irradiated, a gas was evolved which was identified by laser Raman spectroscopy as CO_2, and a spectrum was observed with *a*(1H) 11.2 G, *a*(2H) 4.2 G, and *g* 2.0028. We ascribe this to the dihydroxymethyl radical (**19**), for which the values *a*(1H) 12.3 G, *a*(2H) 3.5 G, and *g* 2.0031 have been reported, in aqueous solution.[8] Presumably triplet-excited formic acid abstracts a hydrogen atom from a second formic acid molecule, but the singlet spectrum of the hydroxycarbonyl radical (**20**) (*g* 2.0002) was not apparent.[9]

When pentamethylcyclopentadiene was added to the formic acid, a pink solution was obtained, but no gas was evolved on irradiation, and no spectrum relating either to the solvent or the solute was observed.

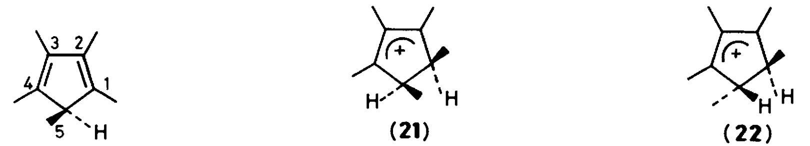
When acetic acid was used as the solvent, irradiation generated the spectrum of the neutral pentamethylcyclopentadienyl radical (**6**), and a gas which was shown to be hydrogen (see later) was evolved.

When sulphuric acid was used as the solvent, a weak spectrum of the radical cation (**7**) slowly developed in the dark,



(8)

Table 2. ^1H N.m.r. chemical shifts of Me_5C_5H in various solvents



	CDCl$_3$	MeCO$_2$H	ClSO$_3$H	CF$_3$CO$_2$H	ClSO$_3$H	CF$_3$CO$_2$H
5-H	2.55(m)	*a*	3.40(br s)	3.27(br d)	2.95(br s)	2.8(br s)
5-Me	1.03(d)	0.87(d)	1.32(d)	1.03(d)	1.39(d)	1.13(d)
4-Me	1.85(s)	1.62(s)	2.75(q)	2.55(br)	2.75(q)	2.55(br s)
3-Me	1.85(s)	1.68(s)	2.10(s)	1.83(s)	2.10(s)	1.83(s)
2-Me	1.85(s)	1.68(s)	2.75(q)	2.55(br)	2.75(q)	2.55(br s)
1-Me	1.85(s)	1.62(s)	1.39(d)	1.03(d)	1.39(d)	1.13(d)
1-H			3.40(br s)	3.80(br s)	2.95(br s)	2.80(br s)

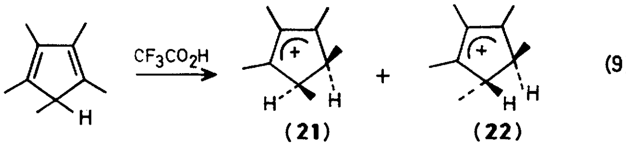
[a] Not observed.

and the intensity was enhanced on irradiation. With fluorosulphonic acid as solvent, no spectrum was observed in the dark, but a rather weak spectrum of the radical cation (**7**) was produced on irradiation.

N.m.r. Spectroscopy.—The ^1H n.m.r. spectra of pentamethylcyclopentadiene in chloroform, acetic acid, and trifluoroacetic acid were recorded, in order to determine the species present in solution. The results are given in Table 2, together with Sorensen's results[10] obtained for solutions in chlorosulphonic acid.

When the solvent is changed from chloroform to acetic acid, the only change in the spectrum is that all the peaks move upfield by *ca.* 0.2 p.p.m. We assume that this is a solvent effect, and that protonation of the diene is insignificant under these conditions.

With trifluoroacetic acid as solvent, however, after 25 min only *ca.* 1% of the free diene could be detected, and the spectrum showed the presence principally of the *cis*- and *trans*-forms [(**21**) and (**22**)] of the protonated diene as identified by Sorensen, the latter in the higher concentration.



(9)

When the solution was irradiated with u.v. light, the only significant change was the appearance of a singlet at δ 1.11.

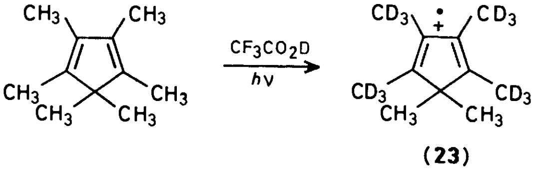
Product Analysis.—When pentamethylcyclopentadiene is irradiated in a neutral solvent, a gas is evolved, and analysis of the gas space by laser Raman spectroscopy shows this to be dihydrogen [equation (2)].[5]

Similar experiments were carried out with the diene in acidic solvents. With acetic acid, gas evolution was obvious, and the Raman spectrum showed it to be hydrogen. Gas evolution was apparent also with difluoroacetic acid, but not with trifluoroacetic acid. Repeated attempts to analyse the gas space were unsuccessful because of fluorescence by these solvents.

Experiments with Trifluoroacetic [^2H]*Acid.*—(i) A solution of pentamethylcyclopentadiene (50 μl) in trifluoroacetic [^2H]acid (500 μl) developed the ^1H n.m.r. signal corresponding to CF_3CO_2H, showing that proton exchange occurred between the solvent and solute within 20 min. After 48 h, the solution was quenched with ice and potassium carbonate, and the organic material was extracted into dichloromethane. Mass spectrometry showed that deuteriation had occurred up to a maximum of [$^2H_{12}$]pentamethylcyclopentadiene. The dehydrodimer, decamethylbicyclopentadienyl, was also detected, deuteriated to a maximum of [$^2H_{24}$]($Me_5C_5)_2$.

(ii) A solution of pentamethylcyclopentadiene (5 μl) in CF_3CO_2D (500 μl) was irradiated in the cavity of an e.s.r. spectrometer; the spectrum shown in Figure 4(a) was obtained. Figure 4(b) shows a construction of the spectrum of the perdeuteriopentamethylcyclopentadiene radical cation based on the known spectrum of $Me_5C_5H^{+\bullet}$ (Figure 1). The correspondence is good but not perfect, and we conclude that deuteriation is extensive though not complete.

(iii) A solution of hexamethylcyclopentadiene (5 μl) in CF_3CO_2D (500 μl) was irradiated in the cavity of an e.s.r. spectrometer; the spectrum shown in Figure 5(a) was observed. Figure 5(b) shows a construction of the spectrum of the [$^2H_{12}$]-radical cation (**23**) based on the analysis of the known spectrum of the perprotio-radical cation (**10**). Again, there is a good correspondence between the observed and constructed spectra.



(10)

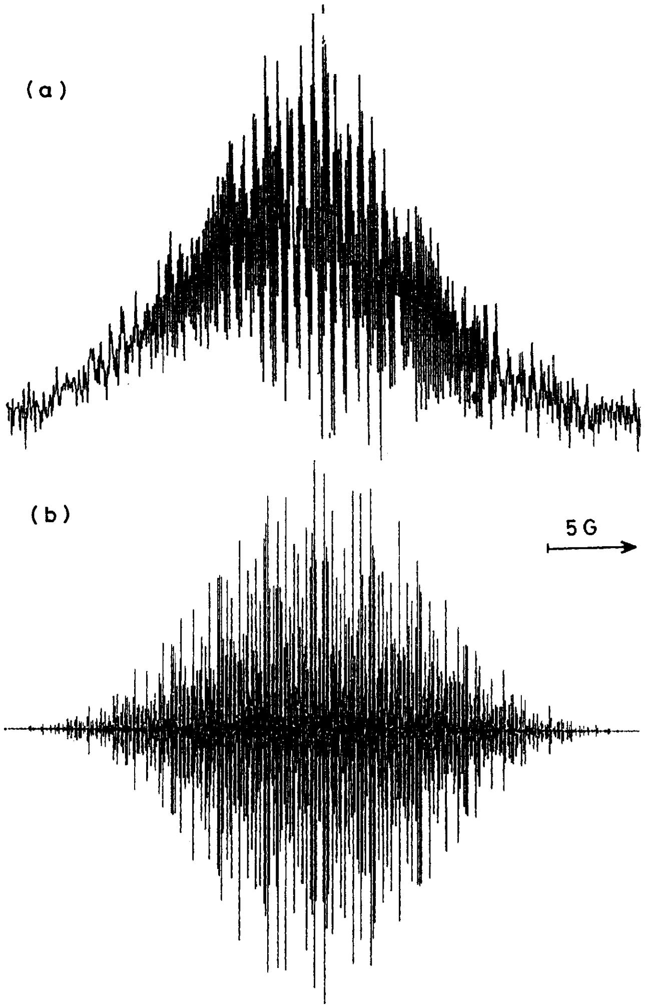


Figure 4. (a) E.s.r. spectrum observed on irradiation of Me_5C_5H in CF_3CO_2D at 262 K; (b) simulation of the predicted spectrum of $(CD_3)_5C_5D^{+\bullet}$

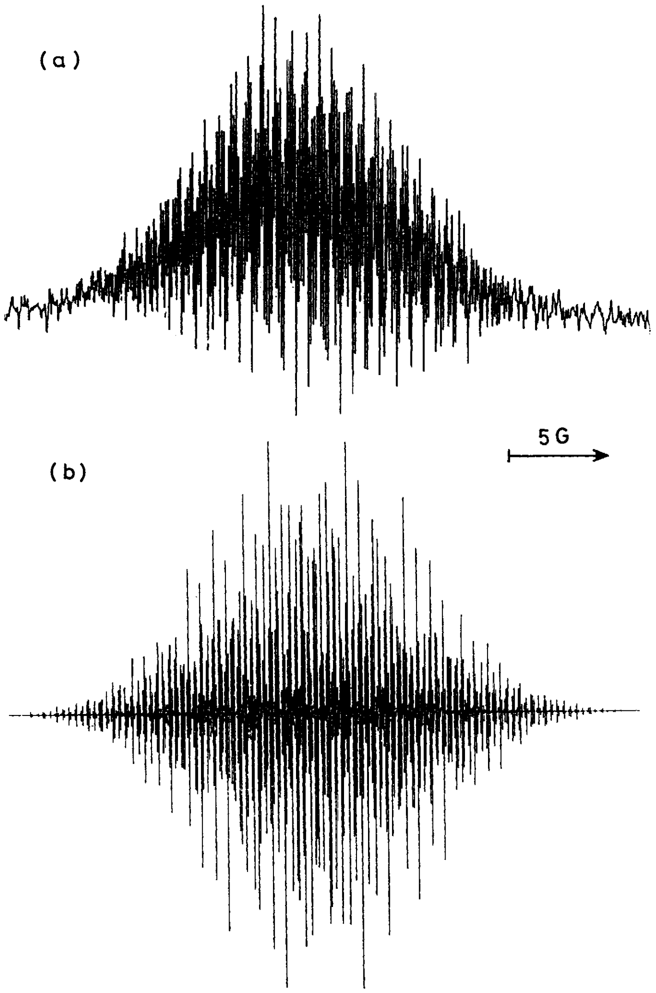


Figure 5. (a) E.s.r. spectrum observed on irradiation of Me_6C_5 in CF_3CO_2D at 264 K; (b) simulation of the predicted spectrum of $(CD_3)_4C_5(CH_3)_2^{+\bullet}$ (**23**)

We conclude that all the allylic methyl groups, but not the *gem*-dimethyl groups, have exchanged with the solvent.

The trifluoroacetic acid was removed at reduced pressure, and the presence of the [$^2H_{12}$]hexamethylcyclopentadiene (**23**) was confirmed by mass spectrometry.

Photochemical Studies.—The u.v. spectrum of pentamethylcyclopentadiene in dichloromethane has an absorption onset at 308 nm and $\lambda_{max.}$ 250 nm. The spectrum in acetic acid is similar, with an absorption onset at 320 nm, although $\lambda_{max.}$ is partially obscured by solvent absorption.

A solution of pentamethylcyclopentadiene in trifluoroacetic acid (*ca.* 10^{-3}M) appears yellow. The spectrum has $\lambda_{max.}$ 295 nm with a weak absorption tail, containing a second weak extinction maximum ($\lambda_{max.}$ 405 nm; ε *ca.* 50), which extends to *ca.* 500 nm. N.m.r. studies (see before) show that such a solution consists almost exclusively of protonated Me_5C_5H.

We conducted experiments with a series of glass optical cut-off filters which passed light with $\lambda > 390$ nm, > 360 nm, > 330 nm (soda glass) and > 300 nm (Pyrex glass). Solutions of pentamethylcyclopentadiene in acetic acid and in trifluoroacetic acid were irradiated in the e.s.r. cavity, and the longest wavelength radiation which could induce radical formation was determined.

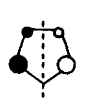
Conversion of Me_5C_5H in CH_3CO_2H into the neutral radical $Me_5C_5^{\bullet}$ [equation (2a)] can only be achieved by light with $\lambda < 330$ nm. In contrast, in CF_3CO_2H, formation of the radical cation $Me_5C_5H^{+\bullet}$ is readily achieved by light of $\lambda > 390$ nm.

Discussion

E.s.r. Spectra.—The SOMO of the cyclopentadiene radical cation has the coefficients given in equation (11), and illustrated

$$\psi_2 = 0.602\,\varphi_1 + 0.371\,\varphi_2 - 0.371\,\varphi_3 - 0.602\,\varphi_4 \quad (11)$$

in (**24**). This leads to the electron densities $q_{1,4}$ 0.362 and $q_{2,3}$ 0.138, or, by the Hückel-McLachlan equation (λ = 1.1), to the spin densities $\rho_{1,4}$ 0.442 and $\rho_{2,3}$ 0.050. If in the McConnell equation we accept a value of Q_{Me} taken from $C_6Me_6^{+\bullet}$ of 39 G, the Hückel model predicts the hyperfine coupling constants *a*(Me-2,5) 14.1 and *a*(Me-3,4) 5.4 G, and the Hückel-McLachlan model predicts the values 18.5 and 1.95 G, respectively.



(**24**)

Comparison of our observed values of a(Me-2,5) 14.4—15.2 G and a(Me-3,4) 4.0 G for the methylated cyclopentadiene radical cations (**7**), (**10**), and (**12**) with these predicted values shows that the agreement is as good as is normally observed for such simple calculations.

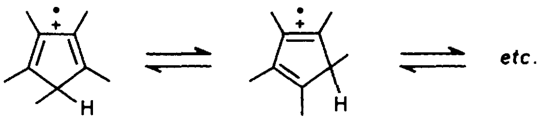
Our observed values for a(Me) can also be compared with those for the acyclic hexamethylbutadiene radical cation (**4**), namely a(Me-1,4) 10.55 and 10.7 G, a(Me-2,3) 4.2 G.[4] The difference between the values for the cyclic and acyclic systems may in part be due to divergence from planarity in the acyclic diene.

The principal distinguishing feature of the cyclic system however is that the sp^3 C-5 and its substituents lie in the nodal plane of the ψ_2 orbital [see (**24**)], resulting in very low (0.8—1.6 G) hyperfine coupling to hydrogen atoms or methyl groups at these positions.

This general spin distribution has already been observed by Shida and his co-workers for the cyclopentadiene radical cation generated in a Freon matrix by γ-irradiation;[11] their observed values for a(H-1,4), a(H-2,3), and a(2H-5) correlate with our corresponding values for a(Me) and are included in Table 1.

A further interesting feature of the e.s.r. spectra concerns the possibility of detecting molecular fluxionality. In the cyclopentadienes a 1,5-suprafacial shift of hydrogen is symmetry-allowed, but it is slow on the n.m.r. timescale.[12]

A similar sigmatropic rearrangement in the cyclopentadiene radical cations [equation (12)] would also be symmetry-allowed,[13] and if it were rapid on the e.s.r. timescale the spectrum would simplify to a sexadecet of doublets. We observed no change in the e.s.r. spectrum up to 328 K, implying that the rate constant of the rearrangement is less than *ca.* 10^7 s^{-1} at this temperature.



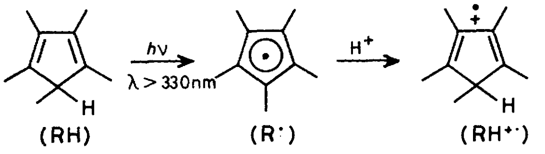
(12)

Mechanism of Oxidation.—^{1}H N.m.r. spectroscopy shows that a solution of pentamethylcyclopentadiene (RH) in trifluoroacetic acid contains *ca.* 1% of the neutral molecule RH, and 99% of the protonated diene (RH_2^+) [equation (9)]. Irradiation of this solution generates the radical cation $RH^{+\bullet}$ [equation (2b)]. The chromophores which potentially could be involved in the primary absorption are therefore the neutral diene (RH), the protonated diene (RH_2^+), and CF_3CO_2H (or $CF_3CO_2^-$) itself.

Since the radical cation is easily generated by irradiation at $\lambda > 300$ nm, we can immediately discount the involvement of photoexcited trifluoroacetic acid in the reaction mechanism, as CF_3CO_2H (or $CF_3CO_2^-$) does not absorb above 280 nm.

The n.m.r. spectrum shows that the diene RH is unprotonated in acetic acid. There is no u.v. absorption above 310 nm, and the neutral radical R$^\bullet$ can be produced only by irradiation with light of $\lambda < 330$ nm. When CF_3CO_2H is the solvent, a strong signal of the radical cation $RH^{+\bullet}$ is observed even upon irradiation at $\lambda > 390$ nm.

The spectra of the neutral diene RH should be similar in CF_3CO_2H and CH_3CO_2H; therefore light of $\lambda > 330$ nm would not be absorbed by the 1% of the diene RH which is present in CF_3CO_2H. This rules out the possibility that the radical cation is formed by CH homolysis in the neutral molecule [equation (13)].



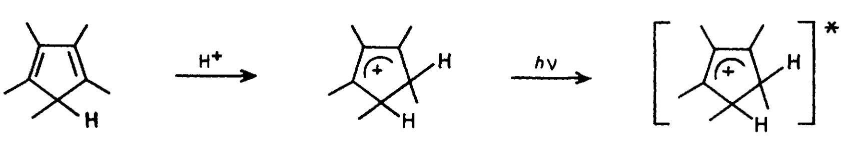
(13)

The u.v.–visible spectrum of the protonated diene RH_2^+ in CF_3CO_2H has a weak absorption which extends to *ca.* 500 nm. Irradiation into this tail with $\lambda > 390$ nm light will result in absorption exclusively by the protonated diene, RH_2^+. Such irradiation produces a strong e.s.r. spectrum of the radical cation, $RH^{+\bullet}$. We therefore conclude that the protonated diene RH_2^+ is the photoprecursor of the radical cation ($RH^{+\bullet}$) in CF_3CO_2H.

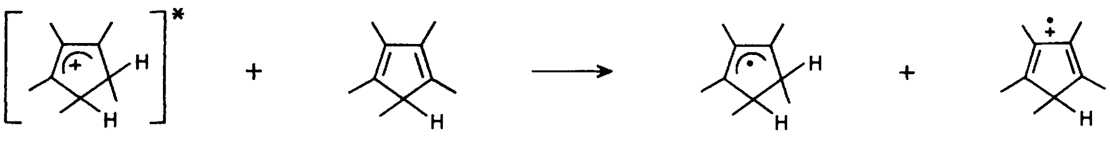
There are two mechanisms by which we envisage photoexcited RH_2^+ could generate a radical cation [equations (15) and (16)]. In reaction (13), the proton in $RH^{+\bullet}$ is derived wholly from the solvent, whereas in reactions (15) and (16) it is derived half from the initial hydrocarbon RH and half from the solvent. Our experiments using CF_3CO_2D as solvent were aimed partly at checking the origin of this proton, but this was frustrated by the rapid exchange of all the hydrogen atoms with the solvent.

Reaction (15) involves electron transfer to RH_2^+ from the small amount of RH which we know from our n.m.r. experiments to be present. A similar process, under non-photolytic conditions, has been considered for the oxidation of arenes to arene radical cations in concentrated sulphuric acid.[14]

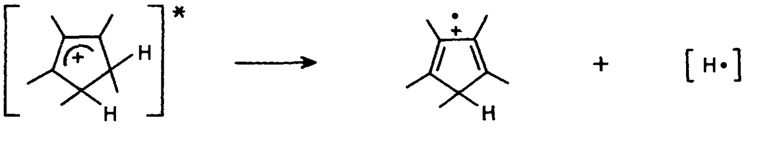
The alternative reaction (16) involves simple unimolecular homolysis of a CH bond in the photoexcited cation RH_2^{+*}, and



(14)



(15)



(16)

is analogous to the mechanism which we proposed initially for the formation of the neutral radical ($R^{\cdot}$) from pentamethylcyclopentadiene [reaction (2a)]. We note however that if the hydrogen atoms were transferred directly to a cyclopentadiene molecule, the products would be indistinguishable from those of equation (15).

Our evidence appears to be compatible with either reaction (15) or (16) and at present we are not able to choose between these two mechanisms.

Conclusion

This work has provided the first examples of the observation of e.s.r. spectra of cyclopentadiene radical cations in liquid solution. It has established the photolysis of a solute in trifluoroacetic acid as a convenient route for generating radical cations, and has shown that, at least in the case of pentamethylcyclopentadiene, the primary photochemical process involves photoexcitation of the protonated diene.

We have subsequently used this technique for oxidising other types of hydrocarbons (*e.g.* di-t-alkylacetylenes to cyclobutadiene radical cations,[15] or azulenes to azulene radical cations [16]), and have recently extended it to the detection of the first radical cations of heterocyclopentadienes, namely the furans, in fluid solution.[17]

Experimental

Cyclopentadiene and methylcyclopentadiene were obtained by thermal cracking of the commercially available dimers (Aldrich). Di-, tri-, tetra-, and penta-methylcyclopentadienes were prepared as described previously.[5] Hexamethylcyclopentadiene, b.p. 32—34 °C at 0.5 mmHg, was obtained in 55% yield from the reaction of pentamethylcyclopentadienylpotassium with methyl iodide;[18] $\delta(^1H)$ ($CDCl_3$) 0.9 (6 H, s, 2 Me) and 1.75 (12 H, br s, 4 Me); $\delta(^{13}C)$ ($CDCl_3$) 9.48 (1,4-Me_2), 10.99 (2,3-Me_2), 21.81 (5-Me_2), 52.22 (C-5), 138.08 (C-1, 4), and 142.35 (C-2, 3).

Decamethylbi(cyclopentadienyl) (**8**) was prepared by the method of Macomber and Rausch.[19]

N.m.r. spectra were recorded using a Perkin-Elmer R12 or Varian XL200 spectrometer, and e.s.r. spectra with a Varian E4 or E109 instrument fitted with a 500 W high-pressure mercury arc focussed on the cavity.

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