The Photolysis of Pentamethylcyclopentadiene: Experiments with Isotopically Labelled Material

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Photolysis of the ^{13}C-labelled pentamethylcyclopentadienes $(^{13}CH_3)(CH_3)_4C_5H$ and $(CH_3)_5{}^{13}CC_4H$ in hexane solution gives the corresponding pentamethylcyclopentadienyl radicals with the e.s.r. parameters $a(^{13}C_\alpha)$ 2.68 and $a(^{13}C_\beta)$ 3.35 G; this confirms that these are π-delocalised radicals which can be treated by π-electron theory. Photolysis of various deuterium-labelled pentamethylcyclopentadienes shows that, in the dihydrogen which is evolved, one hydrogen atom is derived from the CH of the ring and the other from a CH_3 group, rather than both from the ring. The use of Raman spectroscopy as an easy and effective method for the analysis of the isotopic composition of dihydrogen is described.

We have shown recently that, when pentamethylcyclopentadiene (I) is irradiated with u.v. light, hydrogen is evolved and the e.s.r. spectrum of the pentamethylcyclopentadienyl radical (II) can be observed (Scheme 1).[1,2] Decamethylbi(cyclopentadienyl) (III) and tetramethylfulvene (IV) are the principal organic products, and, if the reaction is carried out in ethylene as solvent, the spectrum of the ethyl radical is observed. We suggested that the photolysis involved unimolecular homolysis of the sp^3 C–H bond to give the radical (II) and a hydrogen atom, and then, in the absence of other reagents, this was followed by attack of the hydrogen atom at hydrogen in the same bond of a second molecule of (I).

A similar phenomenon has subsequently been observed with other alkylcyclopentadienes, $R_nC_5H_{6-n}$, $n = 0$, 3, 4, and 5, viz. C_5H_6,[3] 1,2,3-$Me_3C_5H_3$, 1,3,4-$Me_3C_5H_3$, 1,2,3,4-$Me_4C_5H_2$,[4] 1,2,3,4-Me_4-5-R^1C_5H (R^1 = Et, Pr, or Bu),[5] 1,3,4-Me_3-2,5-Et_2C_5H,[5] and 1,2,3,4,5-Et_5C_5H.[6]

These processes are important for two reasons. First, such photosensitivity in a family of hydrocarbons is unprecedented, and has implications in thermochemistry. Secondly, the cyclopentadienyl system appears to provide the smallest neutral annulene radicals to which π-electron theory may be applied.[4] We have therefore extended this study to the photolysis of

various ^{2}H and ^{13}C isotopomers of (I). The results provide a deeper understanding of the e.s.r. spectrum and the molecular and electronic structure of the radical (II), and require some modification to the picture of the origin of the dihydrogen in Scheme 1.

Results and Discussion

Preparation of ^{13}C and ^{2}H Labelled Pentamethylcyclopentadienes.—The preparations of the various isotopically labelled cyclopentadienes are illustrated in Schemes 2—4. Products were purified by preparative g.l.c. and characterised by mass spectrometry and/or n.m.r. spectroscopy. Mass spectrometry and e.s.r. spectroscopy showed that the isotopic labelling in $(CH_3)_4(CD_3)C_5H$ was ca. 85%, although the starting CD_3I was 99% isotopically pure. We believe that the final elimination of water gives some 2,3-dihydrofulvene, which rearranges to $(CH_3)_4(CD_2H)C_5H$.

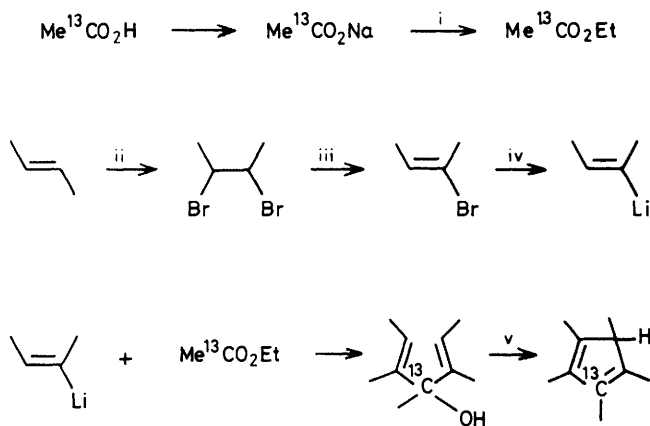*E.s.r. Spectra of ^{13}C-Labelled Me_5C_5·.*—The strongest e.s.r. spectrum of the Me_5C_5· radical (g 2.0025) can be observed from the photolysis of $(Me_5C_5)_2Hg$ or $Me_5C_5P(S)(OMe)_2$. The spectrum from the former route is illustrated in ref. 1; satel-
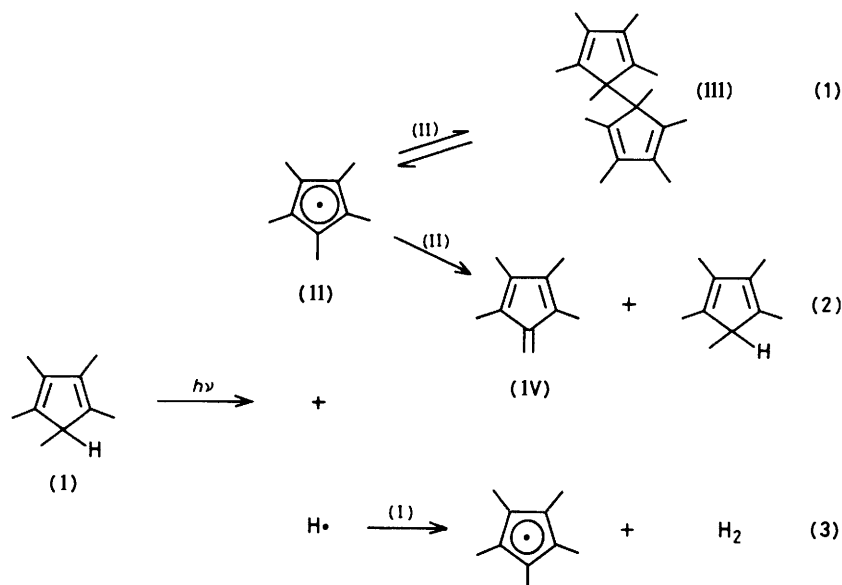
Scheme 1.
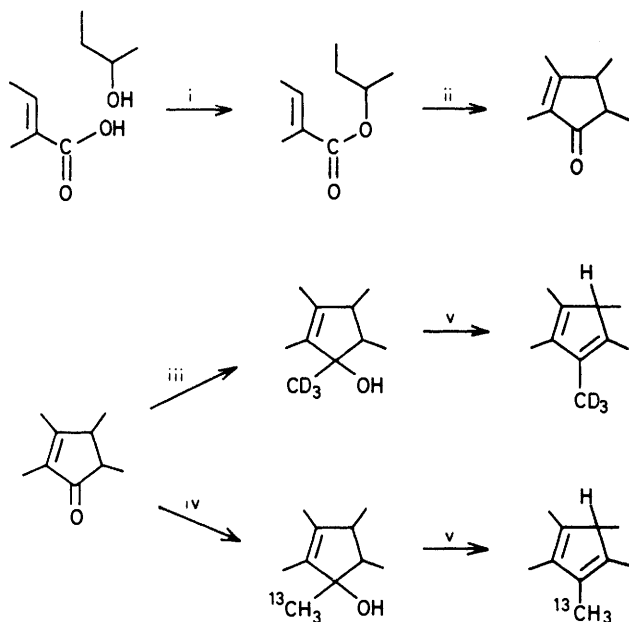
Scheme 2.[7] *Reagents*: i, H$^+$; ii, P$_2$O$_5$; iii, CD$_3$MgI; iv, ^{13}CH$_3$MgI; v, I$_2$

Me^{13}CO$_2$H ⟶ Me^{13}CO$_2$Na $\xrightarrow{\ i\ }$ Me^{13}CO$_2$Et

Scheme 3.[8,9] *Reagents*: i, Et$_2$SO$_4$; ii, Br$_2$; iii, KOH; iv, Li; v, Ar-SO$_3$H

lites due to ^{13}C hyperfine coupling can readily be observed, but they could not be resolved into possible contributions from the α (ring) or β (methyl) carbon atoms,* and it is not clear how the coupling should be assigned. Persistent, stronger spectra can be obtained by photolysing a suspension of solid Me$_5$C$_5$Li,[2] but the lines are broader and the satellites are less easy to distinguish.

The individual contributions of the ^{13}C$_\alpha$ and ^{13}C$_\beta$ hyperfine coupling however can readily be identified by use of isotopically labelled radicals.

The central pair of principal lines in the spectrum of the Me$_5$C$_5$· radical from the photolysis of Me$_5$C$_5$H in hexane is shown in Figure 1a; on this expansion, it is difficult to identify the satellites.

The same central region of the spectrum which is observed

* The positions of atoms relative to the radical centre are denoted by the labelling H–Ċ–C–H.

α α β β
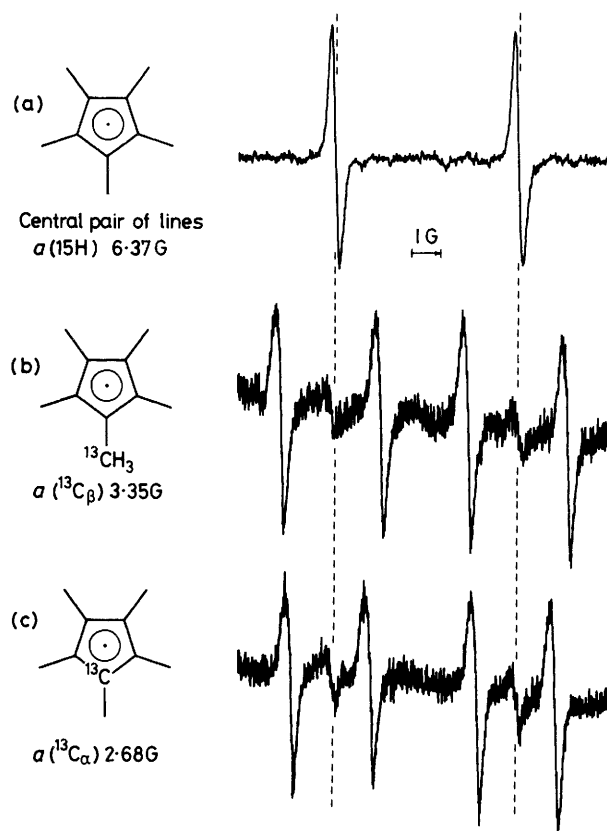
Scheme 4. *Reagents*: i, BuLi; ii, D$_2$O

Me$_5$C$_5$H $\xrightarrow{\ i\ }$ Me$_5$C$_5$Li $\xrightarrow{\ ii\ }$ Me$_5$C$_5$D

(a)

Central pair of lines
a(15H) 6·37G

(b)

^{13}CH$_3$

a(^{13}C$_\beta$) 3·35G

(c)

^{13}C

a(^{13}C$_\alpha$) 2·68G

Figure 1. E.s.r. spectra of the radicals (CH$_3$)$_5$C$_5$·, (^{13}CH$_3$)(CH$_3$)$_4$C$_5$·, and (CH$_3$)$_5$^{13}CC$_4$· in hexane at −25 °C

when (^{13}CH$_3$)(CH$_3$)$_4$C$_5$H is photolysed is shown in Figure 1b, and can be correlated with Figure 1a by the presence of the weak lines due to the residual 10% of unlabelled material; the doublet coupling from ^{13}C$_\beta$ is seen to be 3.35 G. The spectrum from the photolysis of (CH$_3$)$_5$(^{13}CC$_4$)H is illustrated similarly in Figure 1c, where a(^{13}C$_\alpha$) can be identified as 2.68 G.

We will discuss first the value of a(^{13}C$_\alpha$).

Hyperfine coupling to carbon in an annulene ring was first analysed by Karplus and Fraenkel,[10] by considering the spin polarisation of the 1s electrons, and of the electrons in the three σ-bonds, by the unpaired spin density in the p-orbital on the carbon atom in question, and on the attached carbon atoms. This analysis is poor for angle-strained annulenes, for which the related Yonezawa–Kawamura–Kato treatment[11] gives better results. INDO calculations, which are parametrized on a broader basis, are usually less satisfactory.[12]

The results of calculations by these three methods, together with the observed hyperfine coupling constants, are shown in Table 1.

The value of a(^{13}C$_\alpha$) of 2.68 G which we observe for the Me$_5$C$_5$· radical is close to that of 2.6 G (see Table 1) observed for C$_5$H$_5$· and confirms unambiguously that pentamethylation has not changed the π-character of the radical. This was not a foregone conclusion, since trimethylation of the methyl radical to give the t-butyl radical converts a planar species into one which is distinctly pyramidal, though easily inverted.[13] This pyramidization minimises torsional interactions between the

Table 1. Calculated and observed hyperfine coupling constants, $a(^{13}C)$, in annulene radicals

Ring system	Substituents	K.F.[a]	Calc. $a(^{13}C_\alpha)$/G Y.K.K.[b]	INDO[a]	Obsd. $a(^{13}C_\alpha)$/G	Ref.
(3-ring)	Bu$^t_3$	+2.6			30[d]	e
(5-ring)	H$_5$	+1.6	+2.0	+4.1	2.6	f
(6-ring)	H$_6$	+1.3	+2.3	+4.0	2.8	g
(7-ring)	H$_7$	+1.1	+1.8	+3.5	2.2	h
(8-ring)	H$_8$	+1.0	+1.4	+3.0	1.28	i

[a] Karplus-Fraenkel.[10] [b] Yonezawa-Kawamura-Kato.[11] [c] Taken from ref. 14. [d] Concluded to be a σ-radical. [e] Ref. 15. [f] Ref. 16. [g] Ref. 17. [h] Ref. 18. [i] Ref. 19.

(V)
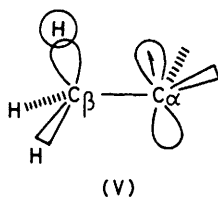
methyl groups and the radical centre, and maximises hyperconjugative stabilization of the radical as shown in (V).[20]

It is also worth noting that the only simple 3-annulene radical for which the e.s.r. spectrum has been observed is tri-t-butylcyclopropenyl, which shows $a(^{13}C_\alpha)$ 30 G (see Table 1), and which is therefore identified as a σ-radical.*[14] This result is normally considered to be due to the effect of angle strain in the three-membered ring, which can accommodate the smaller angle of sp^3 hybridization (109.5°) more readily than that of sp^2 hybridization (120°), but it would nevertheless be interesting to confirm that the C_3H_3· radical itself is similarly a σ-radical, and that the non-planarity in Bu$^t_3C_3$· is not an extreme example of the perturbation of an otherwise planar structure by the three t-butyl substituents.

We conclude that the Me$_5C_5$· radical is a planar π-radical. This justifies the application of π-electron theory to the pentaalkylcyclopentadienes (as has already been done [4,5]), and is

* The arylcyclopropenyls appear to be planar π-radicals[21] but this planarity may be induced by benzylic delocalization of the unpaired electron into the aromatic ring.

Table 2. Hyperfine coupling constants, $a(H_\alpha)$ and $a(C_\beta)$, and the relative McConnell Q values, for carbon-centred π-radicals

Radical	$a(H_\alpha)$/G	$a(C_\beta)$/G	Q_H/Q_C	Ref.
H$_3$C·	22.8			a
CH$_3$CH$_2$·	22.4	13.6	1.65	b
(CH$_3$)$_2$CH·	22.1	13.2	1.67	c
(Me$_3$C)$_2$CH·	21.89	12.25	1.79	d
CH$_3$ĊHCOCH$_2$Me	18.6	10.1	1.84	e
C$_5$H$_5$·	6.0			f
			1.79	
(CH$_3$)$_5C_5$·		3.35		g

[a] Ref. 22. [b] Ref. 23. [c] Ref. 24. [d] Ref. 25. Any hyperconjugative contribution to $a(C_\beta)$ might be different in this compound. [e] Ref. 26. [f] Ref. 16. [g] This paper. No allowance has been made for the fact that hyperconjugative delocalisation of the unpaired spin into the methyl groups of Me$_5C_5$· will reduce ρ_C below the value of 0.2 which it has in C_5H_5·.

relevant to the discussion of the hyperfine coupling to C$_\beta$, which now follows.

Hyperfine coupling to H$_\alpha$ in a planar alkyl radical occurs by spin polarisation of the electrons of the C–H σ-bond, and is described by the McConnell equation (4), where ρ_{C_α} is the spin

$$a(H_\alpha) = \rho_{C_\alpha}Q_H \quad (4)$$

density on C_α and Q_H is the McConnell proportionality constant.

Hyperfine coupling to C$_\beta$ in a methyl substituent will similarly involve spin polarisation of the C_α–C$_\beta$ σ-bond, modified by hyperconjugative interaction with the C$_\beta$–H$_\beta$ bonds. The net effect should still be proportional to the spin density on C_α, as described by equation (5).

$$a(C_\beta) = \rho_{C_\alpha}Q_C \quad (5)$$

Although the values of Q_H and Q_C may vary with the nature of the radical (as they do in, for example, the corresponding arene radical anions and cations), the ratio Q_H/Q_C might be expected to stay approximately constant.

Few data appear to be available in the literature to test this contention. The methyl substituents may render knowledge of ρ_{C_α} ambiguous by reducing the symmetry of the distribution of the unpaired spin over various C_α sites (e.g. as in MeC$_5H_4$·), or by removing spin density from C_α by hyperconjugation (e.g. as in MeCH$_2$·), and they may also confer some σ-character on the radical (e.g. as in Me$_3$C·). However, for planar substituted alkyl radicals MeHĊX, though ρ_{C_α} and hence absolute values of Q_H and Q_C may be questionable, relative values of Q_H and Q_C can be derived by equation (6).

$$a(H_\alpha)/a(C_\beta) = Q_H/Q_C \quad (6)$$

Some relevant data are listed in Table 2. It will be seen that, for the few compounds for which the data are available, Q_H/Q_C lies between the limits of 1.65 and 1.85; relationship (6) may be useful for locating and identifying ^{13}C satellites so that further data of this type can be accumulated.

The Origin of the Hydrogen.—Various deuterium-labelled pentamethylcyclopentadienes were photolysed in hexane solvent, and the gas which was evolved was analysed by laser Raman spectroscopy. Typical spectra, which consist of pure rotational Stokes lines (100—1 100 cm^{-1}) of the H$_2$, HD, and D$_2$ which were evolved, are shown in Figures 2a—d.

Figure 2a shows the characteristic Raman spectrum of the H_2 which is formed when Me_5C_5H is photolysed in hexane. Under the same conditions, Me_5C_5D containing some Me_5C_5H shows the same lines for H_2, together with those for HD, but none for D_2 (Figure 2b); reaction (3), which we initially thought was responsible for the formation of the dihydrogen, is therefore excluded.

Photolysis of Me_5C_5H in perdeuteriocyclohexane gave only H_2 and no HD; the solvent is therefore not chemically involved in the reaction, one hydrogen atom of the dihydrogen apparently being derived from the CH group in the ring, and the other from a CH_3 substituent. This was confirmed by the formation of HD, together with H_2, from $(CD_3)(CH_3)_4C_5H$ (Figure 2c), and D_2 and DH from $(CD_3)(CH_3)_4CD$ (Figure 2d) [together with some H_2 from $(CD_3)(CH_3)_4CH$ impurity].

In principle, the two constituent atoms of the dihydrogen could be derived intramolecularly or intermolecularly from the pentamethylcyclopentadiene. In an attempt to determine the relative significance of these two processes, an equimolar mixture of $(CD_3)(CH_3)_4C_5H$ and $(CH_3)_5C_5D$ was photolysed in hexane, when D_2 could be formed only by an intermolecular process. Only H_2 and HD were in fact detected but this cannot be taken to exclude the intermolecular reaction, as the statistical factor of 18 : 1, together with any isotope effect, might place the concentration of D_2 below the limit of detection.

Our initial proposal for the mechanism (Scheme 1) therefore needs to be modified to accommodate the isotopic composition of the dihydrogen.

It seems likely that some of the dihydrogen is formed by interaction of the primary radicals within the solvent cage [equation (7)], but all the fulvene (IV) cannot arise from this route because we have shown that thermolysis and photolysis of the dehydrodimer (III) produces the fulvene (IV). Reaction (2) therefore still seems to be necessary.
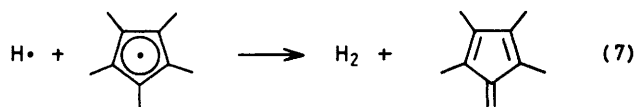
Some radicals must escape from the cage to account for the fact that we see a strong spectrum of the $Me_5C_5\cdot$ radical (II), which decays by a second-order process,[2] presumably involving the bimolecular reactions (1) and (2) which produce the dehydrodimer (III) and some of the fulvene (IV).

This leaves, in the absence of reaction (3), the question of the fate of the hydrogen atom which escapes from the cage, and which can react with ethylene but not perdeuteriocyclohexane solvent. The spectrum of the $Me_5C_5\cdot$ radical which is observed is ' clean ',*,1 but this does not exclude the presence of low concentrations of other short-lived radicals in which the total intensity of the spectrum may be distributed between many lines.

Abstraction of hydrogen from an allylic methyl group in the parent cyclopentadiene (I) would give such a radical [e.g. (V)] which, by loss of [H·] (though not to H·), would serve as a further source of some of the fulvene [equation (8)].

Alternatively, though it seems less likely, the hydrogen atom could add to the diene system of the cyclopentadiene (I) to give the allylic radical (VI), which, by combination with the other radicals present, could lead to the formation of dihydro- or tetrahydro-derivatives of the dehydrodimer (III).

The absence of any detectable attack of hydrogen atoms on
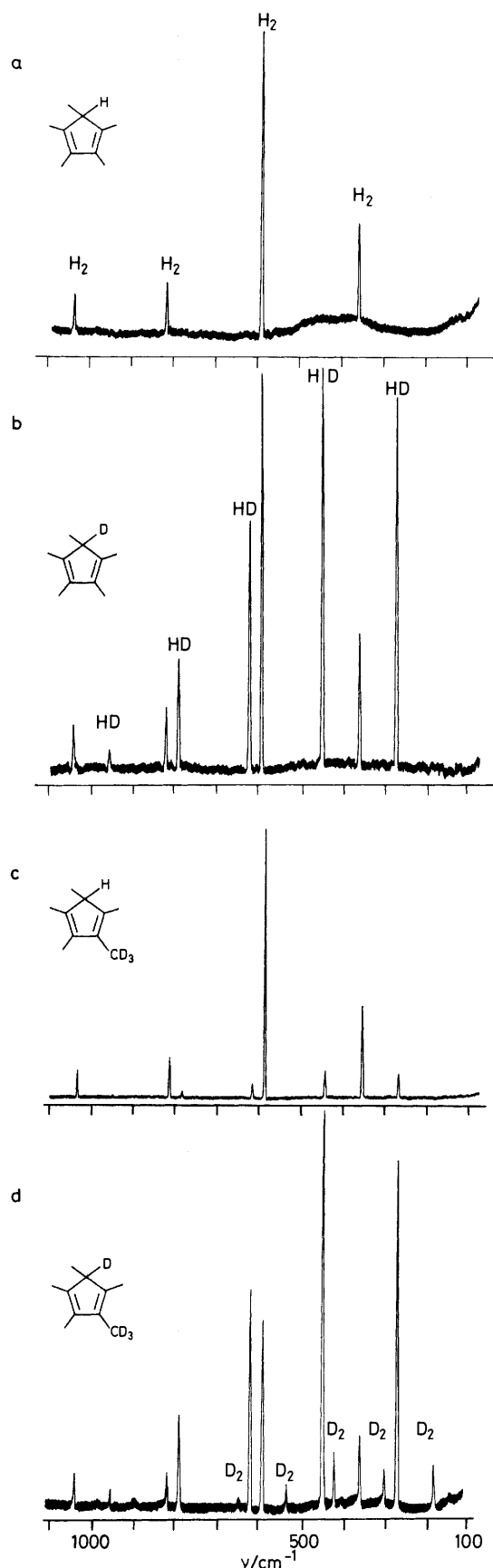
Figure 2. Raman spectra of the dihydrogen evolved from the photolysis of deuteriated pentamethylcyclopentadienes in hexane at room temperature

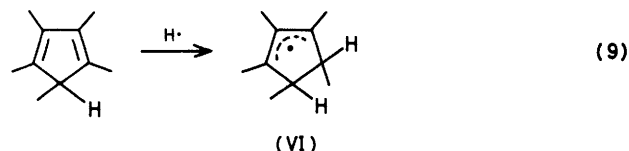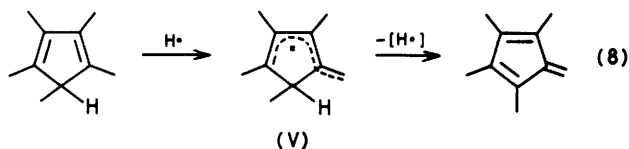* Prolonged photolysis of $(CH_3)_5C_5D$ shows also a weak spectrum of $(CH_3)_4(CH_2D)C_5\cdot$, which probably arises from addition of D· to the fulvene which is formed.

(V)   (8)

(VI)   (9)

This method to determine the isotopic composition of the dihydrogen evolved from a reaction, and thereby to follow the reaction mechanism, has not to our knowledge been used previously: it is remarkably effective, not only in terms of the unambiguous nature of the information obtained, but also in terms of the ease with which the analysis can be carried out and the very small amount of gas required (*ca.* 1 mm^3 at 1 atm. pressure). Moreover, there is no need to remove the gas from the sealed sample tube and all the sample (both liquid and gas) remains undegraded after the analysis and available for further experimentation. The method depends on the high scattering cross-section of hydrogen and on the unique nature of the pure rotational spectrum of H_2, HD, and D_2, specifically the $S_0(J)$ lines (for which $\Delta J = 2$). The most intense lines to follow in this context are the $J = 0$—3 lines of H_2, $J = 0$—4 lines of HD, and $J = 0$—4 lines of D_2, all of which lie in the 150—1 050 cm^{-1} range.[27] Not only the wavenumbers but also the relative intensities of the lines (the latter depending on nuclear spin effects) uniquely define the isotopic composition of the gaseous reaction products.

hydrogen bonded to the ring [reaction (3)] is rather surprising. It might imply that the principal source of dihydrogen is an intramolecular process involving a synchronous elimination or a radical-pair process [equation (7)]; * intermolecularly, the attack of hydrogen atoms at the allylic hydrogen atoms of the methyl groups [equation (8)] is favoured over attack at hydrogen joined to the ring [equation (7)] by a statistical factor of 12 : 1, and by any steric inhibition of reaction (3). Apart from this question of the mechanism of formation of the dihydrogen, the other proposals in the original Scheme 1 appear to be confirmed by the experiments with isotopically labelled compounds.

Experimental

Materials.—The isotopomeric cyclopentadienes were prepared by the reactions shown in Schemes 2—4 using the labelled reagents C^2H_3I (99 atom %; Aldrich Chem, Co.), $^{13}CH_3I$ (91.1 atom %; 1.0 g; Prochem B.O.C. Ltd.), CH_3-$^{13}CO_2H$ (90 atom %; 1.0 g; Prochem B.O.C. Ltd), and ^2H_2O (99.8 atom %; Aldrich Chem. Co.).

Intermediates and products were characterised by ^1H n.m.r. and/or g.l.c.-m.s. using a Pye 204 chromatograph and V6 7070G double focusing spectrometer fitted with a Finnegan-Ingos 2400 data system.

Techniques.—The cyclopentadienes in hexane or ether were sealed under vacuum in Suprasil silica tubes (4 × 140 mm) joined to glass (5 × 50 mm) by a graded seal. These samples were then photolysed for *ca.* 10 h in the cavity of a Varian E109 e.s.r. spectrometer fitted with a field-frequency lock, using light from a 500 W high pressure mercury arc, filtered through an aqueous solution of nickel and cobalt sulphates to remove i.r. radiation.

To analyse the gas which was evolved, the space above the liquid in the still sealed e.s.r. tube was irradiated at 20 °C by a single pass of *ca.* 50 mW of the 514.5 nm line of a Coherent CR3 argon ion laser. The Raman spectra were recorded on a Spex 1401 spectrometer employing a RCA C31034 photomultiplier tube and Bausch and Lomb 1200 line mm^{-1} gratings blazed at 500 nm. The scanning rate (25 cm^{-1} min^{-1}) and spectral slit width (*ca.* 1.5 cm^{-1}) were such that the peak signal count rate was 2 000—5 000 count s^{-1}.

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* Dr. Chen has informed us that when cyclopentadiene is irradiated at 254 nm during deposition in an argon matrix (molar ratio *ca.* 1 : 500) at 4.2 K, the product shows the e.s.r. spectrum of the hydrogen atom and of the cyclopentadienyl radical. This provides some support for the formation of free hydrogen atoms in our system (T. Chen, Thesis, ETH, Zurich, 1981).

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