Photolysis of the Carbon–Hydrogen Bond in Pentamethylcyclopentadiene. Properties of the Pentamethylcyclopentadienyl Radical

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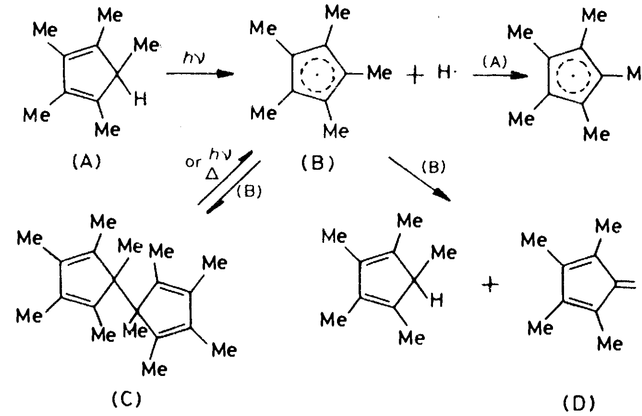
Irradiation of pentamethylcyclopentadiene (A) in liquid solution with u.v. light results in homolysis of the ring C–H bond to give the pentamethylcyclopentadienyl radical (B) [*a* (15 H) 6.4, *a*(^{13}C) 3.5 G], and atomic hydrogen which abstracts hydrogen from a second molecule of (A) to give molecular hydrogen and a second radical (B). The radicals (B) self-react at a diffusion-controlled rate ($2k_t$ 2 × 10^9 l mol^{-1} s^{-1} in hexane at 25 °C) by two different routes. The first, which is thermally and photolytically reversible, is the combination to give the dehydrodimer (C), and the second, which is irreversible, is the disproportionation to give the parent cyclopentadiene (A) and the tetramethylfulvene (D).



We have recently shown that the cyclopentadienyl derivatives of certain metals are photosensitive and irradiation of these compounds in liquid solution with u.v. light in the cavity of an e.s.r. spectrometer shows the spectrum of the cyclopentadienyl radical [equation (1)].

$$C_5H_5ML_n \xrightarrow{h\nu} C_5H_5\cdot + \cdot ML_n \qquad (1)$$

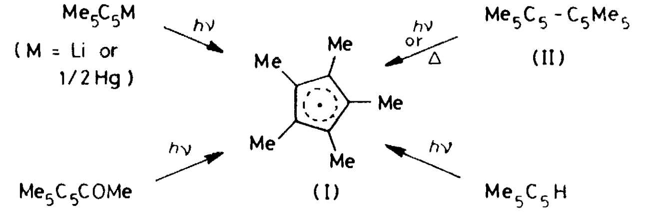
$$M = Li,^{1,2}\ Na,^{2}\ Sn^{II},\ Sn^{IV},^{1,3},\ Hg^{1}\ Pb^{II},\ Pb^{IV},^{4}\ Ti^{IV},\ Zr^{IV\ 5}$$

The derivatives of mercury [1] and of tin [1,3] have been investigated most thoroughly. Introduction of one methyl group into the cyclopentadienyl ring of the tin compounds greatly reduces the photosensitivity, but the photolysis of bis(methylcyclopentadienyl)mercury still shows a strong spectrum of the methylcyclopentadienyl radical.[1]

In view of the increasing importance of the pentamethylcyclopentadienyl group as a ligand for metals, we began a study of the photolysis of pentamethylcyclopentadienyl metal compounds, but it soon became apparent that the parent hydrocarbon itself is remarkably, if not uniquely, photosensitive.

In this paper we concentrate attention on the photolysis of pentamethylcyclopentadiene and on the properties of the pentamethylcyclopentadienyl radical which is formed. We hope to return to the question of the behaviour of the metal derivatives at a later date.

Generation of the Pentamethylcyclopentadienyl Radical.—The e.s.r. spectrum of the $Me_5C_5\cdot$ radical (I) was observed from the six different routes shown in Scheme 1. A suspension of pentamethylcyclopentadienyl-lithium in tetrahydrofuran showed a persistent weak spectrum of the $Me_5C_5\cdot$ radical trapped in the solid matrix, as soon as the sample was inserted into the cavity, and before it was irradiated. It is possible that the compound may be sensitive to the laboratory light, but, more probably, the radical results from oxidation by adventitious oxygen. Irradiation of this suspension gave a very strong spectrum of the matrix-isolated radical (ΔH_{pp} 0.5 G) which persisted for some days at room temperature. Irradiation with u.v. light of a dilute solution of the lithium derivative in tetrahydrofuran showed a stronger spectrum of the radical (I), which disappeared immediately the light was shuttered. For comparison, u.v. irradiation of a solution or suspen-



Scheme 1

sion of cyclopentadienyl-lithium shows the e.s.r. spectrum of the $C_5H_5\cdot$ radical, but, in the presence of oxygen, the persistent spectrum of the fulvalene radical anion is observed.[2]

A stronger spectrum of the radical (I) was observed when bis(pentamethylcyclopentadienyl)mercury was photolysed in toluene solution, and a mirror of mercury was deposited on the walls of the cell; a typical spectrum is illustrated in Figure 1.

FIGURE 1 E.s.r. spectrum of the pentamethylcyclopentadienyl radical obtained from the photolysis of bis(pentamethylcyclopentadienyl)mercury in tetrahydrofuran at 37 °C. The ^{13}C satellites are arrowed

U.v. irradiation of pentamethylcyclopentadienyl methyl ketone showed the same spectrum of the radical (I), formed by Norrish I fragmentation of the ketone triplet. Similar treatment of cyclopentadienyl methyl ketone shows a relatively weak spectrum of the $C_5H_5\cdot$ radical.[6]

If the above systems were heated to 70—100 °C, none showed the spectrum of the $Me_5C_5\cdot$ radical before photolysis, but all showed the spectrum after photolysis. We present evidence below that this behaviour results from the thermal dissociation of the dehydrodimer (II) which is a decay product of the $Me_5C_5\cdot$ radical. Accordingly, pentamethylcyclopentadienyl-lithium was treated with iodine to give a product which showed a parent peak in the mass spectrum corresponding to the dehydrodimer and which, on heating or photolysis showed the e.s.r. spectrum of the $Me_5C_5\cdot$ radical.

Cyclopentadienyl-lithium itself reacts with iodine to give bi(cyclopenta-2,4-dienyl) but this rearranges at room temperature to give bi(cyclopenta-1,3-dienyl).[7] Bi(cyclohepta-2,4,6-trienyl) dissociates reversibly between 120 and 140 °C to show the e.s.r. spectrum of the cycloheptatrienyl radical, and the bond dissociation energy has been measured to be *ca.* 146 kJ mol^{-1}.[8]

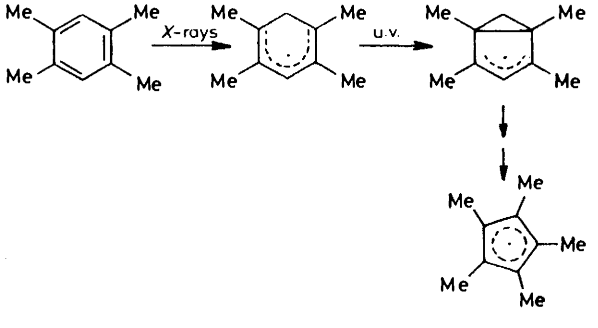
The most interesting route to the radical (I), however, is the photolysis of the parent cyclopentadiene Me_5C_5H as the neat liquid or in hydrocarbon solution; an example of the spectrum which is observed is illustrated in our preliminary communication.[9] Under the same conditions, neither cyclopentadiene nor methylcyclopentadiene show the spectrum of the corresponding radical, but this relative insensitivity to photolysis is only a matter of degree: if the rate of removal of the $C_5H_5\cdot$ radical is greatly decreased by generating it by photolysis of cyclopentadiene as a single crystal or glass, the e.s.r. spectrum of the radical can be observed.[2,10]

This photolysis of pentamethylcyclopentadiene is considered in detail below.

Properties of the Pentamethylcyclopentadienyl Radical.—The e.s.r. spectrum of the pentamethylcyclopentadienyl radical shows (Figure 1) a (15 H) 6.4, a (^{13}C) 3.5 G, g 2.002 5. The inner 14 of the predicted 16 lines due to proton coupling could be identified, in the correct ratio of intensities; the first and sixteenth lines have an intensity of only $1/2^{15}$ *i.e.* 1/32 768 of that of the total spectrum, and could not be detected. The low value of the ^{13}C hyperfine coupling confirms that, like cyclopentadienyl itself [$C_5H_5\cdot$, a (5H) 6.0, a (^{13}C) 2.6 G, g 2.002 5] [1] but unlike the cyclopropenyl analogue [$Bu^t{}_3C_3\cdot$, $a(^{13}C)$ 30.0 G],[11] the $Me_5C_5\cdot$ radical has a π rather than a σ configuration. No evidence for Jahn–Teller distortion could be detected, nor would it be expected, at the temperature of our experiments.

Our results support the assignment to the $Me_5C_5\cdot$ radical of the spectrum [$a(\nless 13$ H) 6.4 G] which Monge and Schott observed when crystalline durene was irradiated first with X-rays and then with u.v. light [equation (2)].[12]

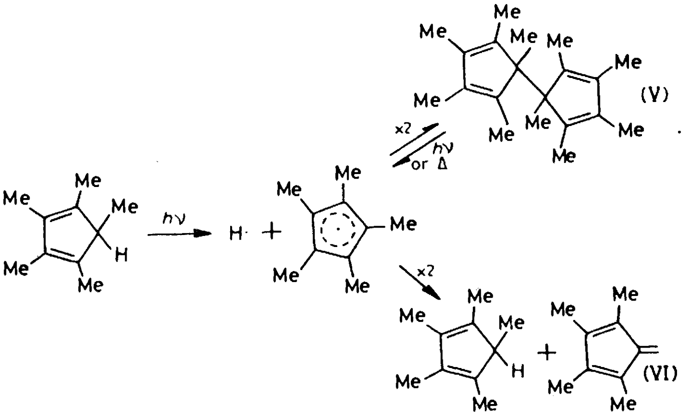
The high concentration of the $Me_5C_5\cdot$ radical which can be obtained from the various routes in Scheme 1 might be taken to imply that the rate of the self-reaction of the radical is unusually low, perhaps because of steric hindrance. However, measurement of the rate constant for this reaction showed that the self-reaction is diffusion-controlled, with $2k_t$ 2×10^9 l mol^{-1} s^{-1} in hexane at 25 °C, close to the value for the cyclopentadienyl radical itself.[2] The relatively high concentrations of the $Me_5C_5\cdot$ radical which can be achieved therefore reflect a high rate of formation rather than a low rate of removal, and seem best ascribed to weakening of the Me_5C_5-X bonds by conjugative and hyperconjugative stabilisation of the $Me_5C_5\cdot$ radical.



(2)

Analysis by g.l.c.-m.s. of the products after photolysis showed the presence of the dehydrodimer (V) (Scheme 2) resulting from the combination of two pentamethylcyclopentadienyl radicals. If the solution after photolysis was heated to 70—120 °C, the dehydrodimer dissociated to restore the spectrum of the radical (I). The compound (V) has been obtained previously by Jutzi and Kohl from the reaction between bis(pentamethylcyclopentadienyl)tin di-iodide and pyridine.[13]

The principal hydrocarbon which was isolated from the photolysis products, however, was the tetramethylfulvene (VI) which does not appear to have been reported previously. Presumably it is formed by the irreversible disproportionation of pairs of radicals (I) formed directly from pentamethylcyclopentadiene or indirectly by dissociation of the dehydrodimer (V).

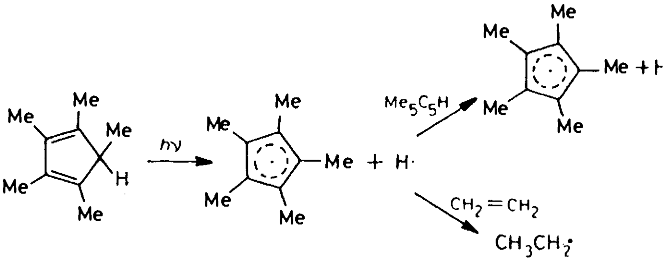


Scheme 2

If the radical (I) was generated between —100 °C and room temperature in the presence of oxygen, a strong singlet was observed, g 2.015 1, ΔH_{pp} 2.0 G, which persisted in the absence of light at low temperature and obviously is to be ascribed to the pentamethylcyclopentadienylperoxyl radical, $Me_5C_5OO\cdot$. It is interesting that despite a number of attempts we have been unable as yet to detect the e.s.r. spectrum of the cyclopentadienylperoxyl radical $C_5H_5OO\cdot$, which by analogy with other cycloalkylperoxyl radicals would be expected to show hyperfine coupling to the γ-proton, $a(H_\gamma)$ 5—7 G.

Photolysis of the C–H *Bond*.—As far as we are aware, there is no precedent for the photolysis of a hydrocarbon RH in solution showing the e.s.r. spectrum of the corresponding radical R·. We have therefore investigated the photolysis of pentamethylcyclopentadiene in more detail to determine whether it involves simple unimolecular homolysis of the C–H bond as illustrated in Scheme 2, or whether some more complex process is involved. All the evidence supports the picture of the simple homolysis.

One alternative might be that photoexcited diene $Me_5C_5H^*$ could abstract hydrogen from unexcited Me_5C_5H to give the radicals $Me_5C_5H_2\cdot$ and $Me_5C_5\cdot$. However, it seems most unlikely that the loss of the radical $Me_5C_5H_2\cdot$ from solution could be faster than that of $Me_5C_5\cdot$ which we have shown (see above) to be diffusion-controlled, and no e.s.r. signals which could be ascribed to the radical $Me_5C_5H_2\cdot$ were observed (Figure 1); furthermore, no products which might result from this radical could be detected.



Scheme 3

The spectrum of hydrogen atoms [a(H) 503.8 G] could not be observed, but none would be expected. In their classic work on the electron irradiation of liquid hydrocarbons, Fessenden and Schuler observed the H· spectrum only from liquid methane at —178 °C.[14] Larger alkanes presumably scavenged the hydrogen atoms by the reactions $RH + H\cdot \longrightarrow R\cdot + H_2$, though some alkenes showed the presence of radicals resulting from the addition of hydrogen to the double bond, *e.g.* $CH_2{=}CH_2 + H\cdot \longrightarrow CH_3\text{-}CH_2\cdot$.

We have given above the arguments for discounting the formation of the adduct $Me_5C_5H_2\cdot$ in our system. The most probable fate of the hydrogen atoms therefore appeared to be their reaction with more parent hydrocarbon Me_5C_5H (or less likely, with the radical $Me_5C_5\cdot$) to give molecular hydrogen and a second radical $Me_5C_5\cdot$ (Scheme 3).

A sample of neat pentamethylcyclopentadiene was therefore sealed under vacuum and photolysed with u.v. light, and any gases which were formed were analysed by g.l.c. and by laser Raman spectroscopy. Hydrogen was identified by g.l.c. and this was confirmed beyond any question by the Raman spectrum shown in Figure 2.

If the photolysis was carried out in liquid ethene as solvent, the hydrogen atom could be observed to react with the solvent, and at −120 to −80 °C a weak spectrum of the ethyl radical (Scheme 3) could be observed.

Although the photolysis of the C–H bond of a hydrocarbon in liquid solution by u.v. light does not appear to have been reported previously we believe that it does occur with certain other compounds, and have detected it, though more weakly, with cycloheptatriene.[15] We hope that reactions of this type may render it possible to generate hydrogen atoms more readily in solution, and to investigate their reactions.

EXPERIMENTAL

Materials.—Hexamethylbicyclo[2.2.0]hexa-2,5-diene (hexamethylDewar benzene) was converted into methyl pentamethylcyclopenta-2,4-dienyl ketone, $\tau(CCl_4)$ 8.18 (2 Me, s, 6 H), 8.33 (6 H, s, 2 Me), 8.46 (3 H, s, Me), and 8.94 (3 H, s, Me),[16] and thence into 1,2,3,4,5-pentamethylcyclopenta-1,3-diene [17] which, for photolytic experiments was purified by preparative g.l.c., $\tau(CCl_4)$ 7.60 (1 H, q), 8.25 (12 H, 4 Me), and 9.05 (3 H, d, *J* 7.5 Hz, Me).

The diene was treated in tetrahydrofuran with butyllithium (1.6M in hexane) to give a suspension of pentamethylcyclopentadienyl-lithium, which reacted with mercuric chloride yielding bis(pentamethylcyclopentadienyl)mercury, $\tau(C_6H_6)$ 8.10 (12 H, s, 4 Me), 8.19 (12 H, s, 4 Me), and 8.73 (6 H, s, 2 Me).[18]

Jutzi and Kohl [13] have questioned the nature of the isolated product [18] as a mercury derivative, pointing out that its characteristics are similar to those of bi(pentamethylcyclopenta-2,4-dienyl).

A suspension of Me_5C_5Li in tetrahydrofuran was treated with iodine. The lithium iodide which was precipitated was filtered off, and the solvent was removed under reduced pressure yielding bi(pentamethylcyclopenta-2,4-dienyl) as a solid which was recrystallised from hexane, *m/e* 270 (M^+).

Techniques.—^{1}H N.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer R12 instrument, or at 200 MHz on a Varian XL 200 instrument.

Samples for e.s.r. spectroscopy were sealed under vacuum in Suprasil silica cells, and thermolysed, or photolysed with light from a high pressure 500 W mercury arc. The solvents used were tetrahydrofuran for Me_5C_5Li, tetrahydrofuran, or toluene for $(Me_5C_5)_2Hg$, and cyclopropane, hexane, toluene, ethylene, or the neat liquid for Me_5C_5H.

The kinetics of removal of the $Me_5C_5\cdot$ radical in solution were measured by computer-averaging of a series of signal decay curves produced by positioning a rotating sector in the light beam.[19,20]

The Raman spectrum of hydrogen was recorded on a Spex 1401 spectrometer, using the 514.0 nm exciting line from a Ar^+ ion laser CR3. G.l.c.–m.s. analysis was carried out with a Pye 204 chromatograph and V6 7070G double focusing mass spectrometer provided with a Finnigan-Ingos 2400 data system.

Products of the Photolysis of Pentamethylcyclopentadiene.—Pentamethylcyclopentadiene in hexane was photolysed in an e.s.r. cell for *ca.* 10 h. A sample of the supernatant gas was analysed by g.l.c. using helium as the carrier gas and a katharometer detector, and showed the unique negative peak due to hydrogen (Perkin-Elmer Sigma 2 instrument fitted with a 8 m column of 60—80 mesh Porapak QS at 25 °C). The Raman spectrum of the gas showed the characteristic vibrational–rotational spectrum illustrated in Figure 2.

The liquid phase was analysed by g.l.c.–m.s. (OV 17 column; temperature range 80—160 °C; electron energy 70 eV; source temperature 160 °C) and showed the presence of the following two products, bi(pentamethylcyclopenta-2,4-dienyl),[13] *m/e* 270 (3%, *M*), 255 (0.2), 137 (11.7), 136 (31.7), 135 (100, *M*/2), 134 (26.6), 119 (11.5), 105 (10.7), and 91 (6.2), and 1,2,3,4-tetramethylfulvene, *m/e* 134 (52.6%, *M*), 133 (14.4), 119 (100), 91 (13.8), 79 (2.9), 77 (5.9), and 65 (3.9); this compound was recovered by preparative g.l.c. as a yellow liquid, $\tau(CDCl_3)$ 4.60 (2 H, s, CH_2), 8.13 (6 H, s, 2 Me), and 8.18 (6 H, s, 2 Me).

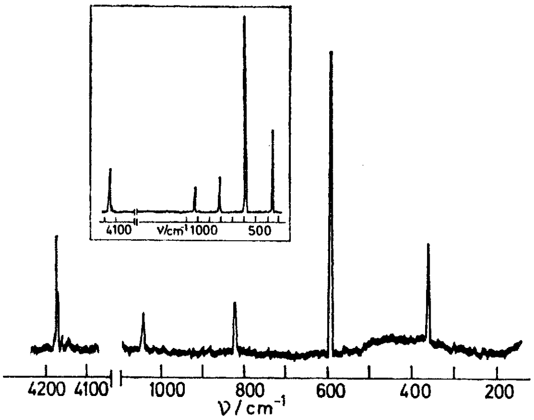


FIGURE 2 Rotation and vibration–rotation spectrum of hydrogen obtained from the photolysis of pentamethylcyclopentadiene. Inset: reference spectrum of hydrogen at 1 atm. pressure

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