The Pentamethylcyclopentadienyl Radical: Generation, Electron Spin Resonance Spectrum, and Reaction Kinetics

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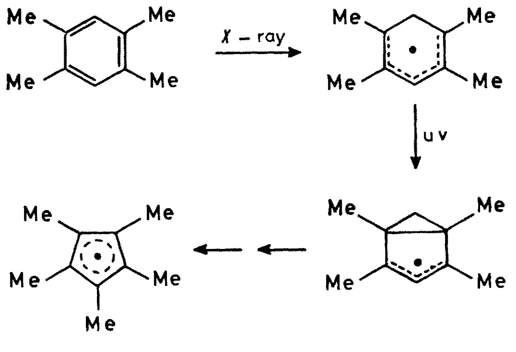
Summary The pentamethylcyclopentadienyl radical [a(15H) 6·4 G, $a(^{13}C)$ 3·5 G, g 2·0025], is formed by the photolysis of pentamethylcyclopentadiene, and undergoes self-reaction at a diffusion-controlled rate ($2k_t$ 2×10^9 l mol^{-1} s^{-1} at 25 °C) to give the dimer which redissociates on heating.

Cyclopentadiene and the monoalkylcyclopentadienes react with t-butoxyl radicals by addition rather than by abstraction of hydrogen, and special organometallic routes had to be developed for generating the radicals C_5H_5• and RC_5H_4• in solution for e.s.r. studies.[1,2] In view of the increasing importance of the pentamethylcyclopentadienyl group as a ligand, we have now investigated the generation of the Me_5C_5• radical, and its e.s.r. spectrum and kinetics of reaction.



Scheme 1

The only previous report of the e.s.r. spectrum of the Me_5C_5• radical is the rather speculative identification of it as the ultimate radical which is observed, with the reasonable hyperfine splitting of $a(\not< 13H) = 6{\cdot}4$ G, when polycrystalline durene is irradiated first with X-rays and then with u.v. light (Scheme 1).[3] In contrast with the difficulty of generating the radicals RC_5H_4•, the radical Me_5C_5• can readily be prepared from a variety of routes such as the photolysis of pentamethylcyclopentadienyl-lithium or methyl pentamethylcyclopentadienyl ketone. The simplest is the photolysis (Scheme 2) of pentamethylcyclopentadiene itself (**1**), when the spectrum of the radical (**2**), as shown in the Figure, is obtained. 14 of the predicted 16 lines can be observed, in the correct ratio of intensities, with a(15H) 6·4 G, $a(^{13}C)$ 3·5 G, and g 2·0025, supporting the assignment in reference 3. The low value of $a(^{13}C)$ confirms that, like the C_5H_5• radical, this is a π-radical with (time-averaged) C_{5h} symmetry.

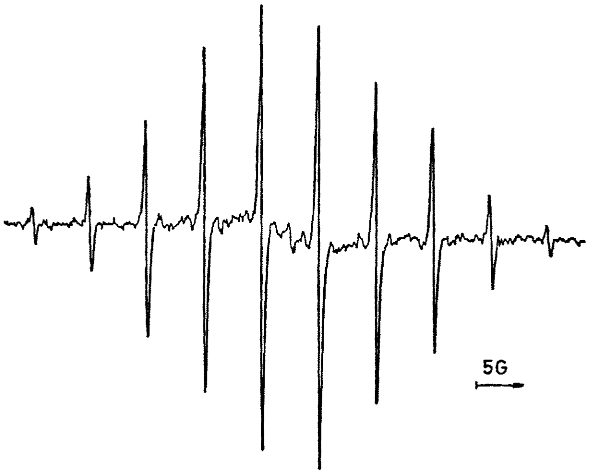
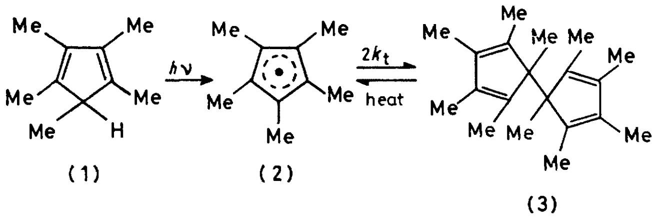


Figure E.s.r. spectrum of the radical Me_5C_5• obtained from the photolysis of pentamethylcyclopentadiene (*ca.* 25% v/v) in hexane at 25 °C.

Under the same conditions, cyclopentadiene and methylcyclopentadiene show no spectra of radicals, and indeed we know of no previous example in which the e.s.r. spectrum of the radical R• has been observed from the photolysis of the hydrocarbon RH.

It seemed possible that the intensity of the spectra might reflect a low rate of removal of the radical by self-reaction because of steric hindrance, but measurement by kinetic e.s.r. spectroscopy showed that, in hexane at 25 °C, $2k_t = 2 \times 10^9$ l mol^{-1} s^{-1}, characteristic of a diffusion-



SCHEME 2

controlled reaction. If the resulting solution is heated to between 70 and 110 °C, the spectrum of the radical (**2**) is regenerated, presumably through dissociation of the dimer (**3**).[4]

The intensity of the spectrum of the radical (**2**) when it is obtained from the hydrocarbon (**1**), or from other routes, therefore results from a high rate of formation of (**2**) rather than a low rate of its removal, and may reflect either the hyperconjugative stabilisation of (**2**) by the five methyl groups, or the more effective absorption of light by the methylated cyclopentadiene (**1**), and its derivatives.

As the removal of the radical $Me_5C_5\cdot$ is close to the diffusion-controlled limit, this would appear to rule out its formation by hydrogen abstraction by photoexcited Me_5C_5H from ground state Me_5C_5H, since the spectrum of the radical $Me_5C_5H_2\cdot$ was not observed, and there seems to be no route by which it could be removed from solution very much more rapidly than $Me_5C_5\cdot$.

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