

PHOTOCHEMISTRY OF CYCLOHEXADIENONE PEROXIDES: STRUCTURE OF THE INTERMEDIATE RADICAL

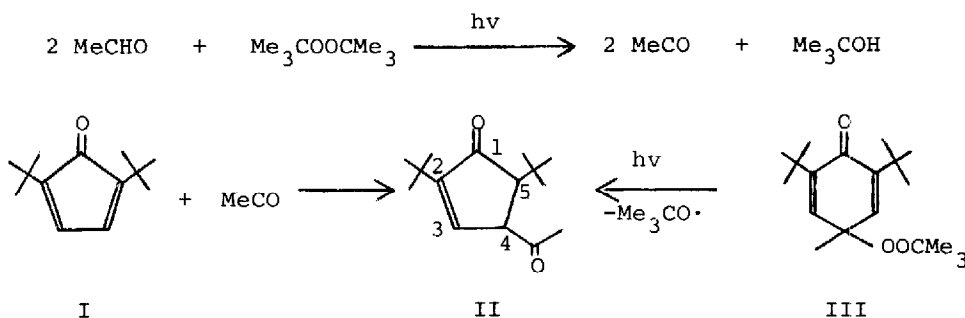
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We have recently tentatively assigned the intermediate radical in the photo-decomposition of 4-t-butylperoxi-4-methyl-2.6-di-t-butyl-2.5-cyclohexadien-1-one (III) the structure of the cyclopentenone-radical II. This structure was compatible with the large number of complex products formed¹⁾

We now confirm our previous assignment having independently generated the identical ESR-spectrum by the addition of acetyl radical to 2.5-di-t-butyl-2.4-cyclopentadien-1-one¹⁾ (I).



Photolysis²⁾ directly in the ESR-cavity of a solution of I ($4 \cdot 10^{-2} \text{M}$) in di-t-butylperoxide and acetaldehyde³⁾ (3 : 7 volume/volume) produced a spectrum (Figure 1) centered at $g = 2.0041 \pm 0.0001$ which we assign to II. It is interpreted in terms of the following coupling constants: $a_1 = (13.97 \pm 0.08) \text{G}$ (1H, C-4), $a_2 = (1.99 \pm 0.02) \text{G}$ (1H, C-3), $a_3 = (0.49 \pm 0.02) \text{G}$ (12H, t-butyl at C-5 and acetyl group at C-4). Within the line width of 200 mG $a_2 = 4a_3$, which leads to the overall appearance of 2 x 17 lines.

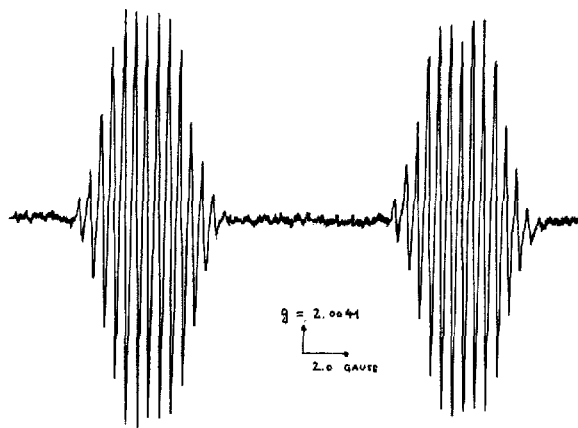
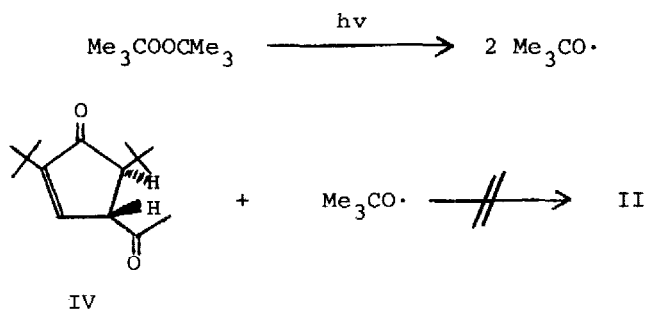


Figure 1: ESR-Spectrum observed on photolysis of a degassed mixture of di-*t*-butylperoxide and acetaldehyde in the presence of I, at 10°C

Further it is of interest to note that irradiation of a solution of 2,5-di-*t*-butyl-4-acetyl-2-cyclopenten-1-one¹⁾ (IV, 10⁻¹M) in di-*t*-butylperoxide did not yield the spectrum of II.



References and Footnotes

- 1) H. Lind, T. Winkler and H. Loeliger in Preprints of the 15th Prague IUPAC-Meeting on Degradation and Stabilization of Polyolefins, 1975, Section F4, J. Polym. Sci., Part C, 14 (1976), in press.
- 2) Using a Philips SP500 high pressure mercury lamp and a Schott WG320 (2mm) filter, 1 : 1 image formation with an f-value $f : 250$.
- 3) The authors thank Prof. H. Fischer, Dept. of Physical Chemistry, University of Zürich for suggesting this method of producing acetyl radicals.