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PHOTOCHEMICAL DECOMPOSITION OF CYCLOHEXA-2,4-DIENONE PEROXIDES

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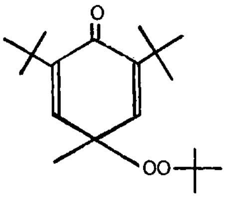
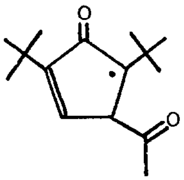
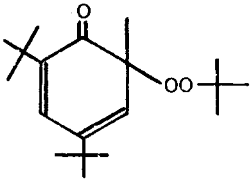
There have been previous reports on the detection[1,2)] and identification[3)] of the cyclopentenone radical II generated photochemically from the peroxycyclohexadienone I. To further confirm the proposed mechanism of formation of II we have studied the photochemistry of orthoalkylperoxy-cyclohexadienone III.


I


II


III

Irradiation[4)] of a 5 x 10^{-2}M solution of 2-t-butylperoxy-2-methyl-2,4-di-t-butyl-2,4-cyclohexadien-1-one[5)] (III) in toluene in the cavity of a VARIAN E-9 spectrometer immediately produced the ESR-spectrum shown in Figure 1A (a_1 = (0.320 ± 0.004)mT (1H), a_2 = (0.199 ± 0.004)mT (1H), a_3 = (0.0377 ± 0.0005)mT (18H) and a_4 = (0.0100 ± 0.002)mT (3H). The spectrum is perfectly simulated (Figure 1B) on a computer utilising the above coupling constants and is assigned to radical structure VI with proton-electron coupling at C-5, C-3, the two t-butyl groups at C-2 and C-4 and the acetyl group at C-5, respectively. The g-value of 2.0034 is in accord with less spin delocalization

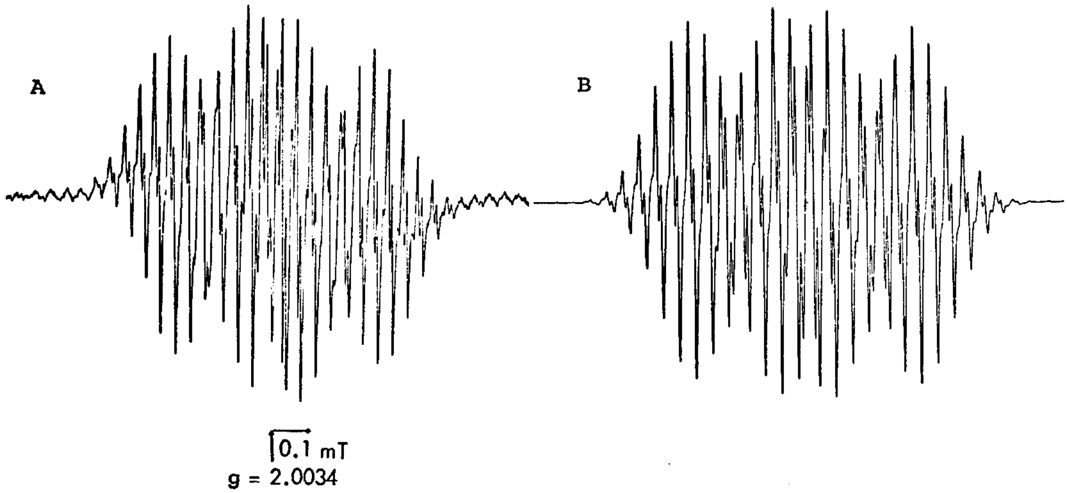
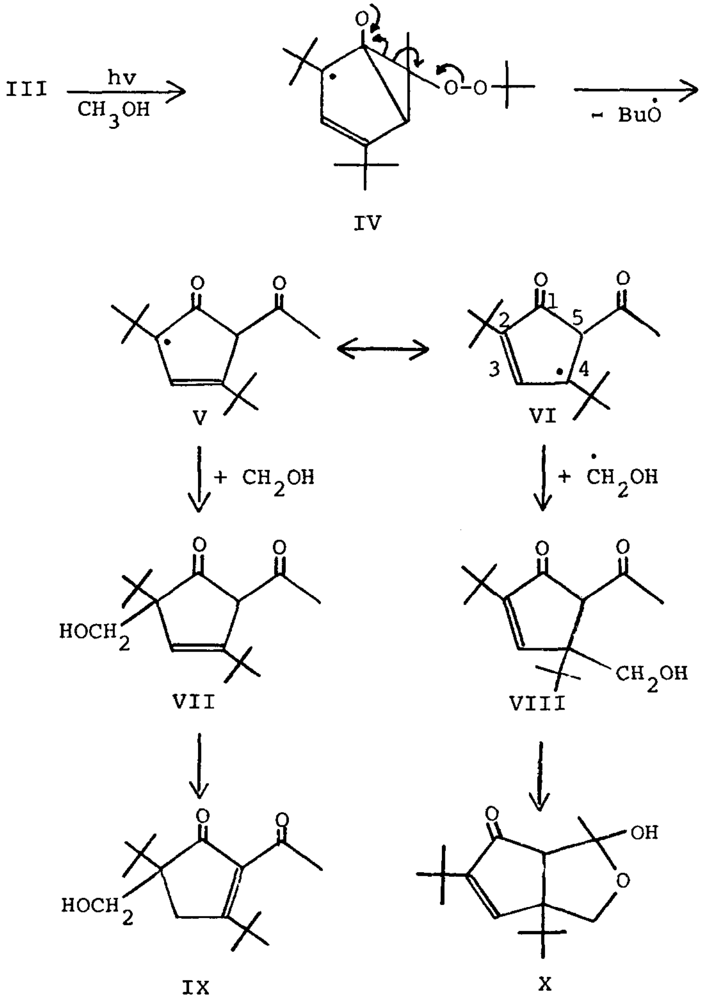


Figure 1: ESR-spectrum generated on photolysis of III in toluene at 10° C, degassed[4] (A) and on computer simulation (B).

at the ring carbonyl group at C-1 in VI than in II. Radical VI had a half-life of around 6 minutes at 10° C in the dark.

We find that continued irradiation of III in toluene causes its slow disappearance and leads to complex product mixtures. However, on photolyzing[6] 7.5×10^{-3}M III in methanol solution and preparative-tlc (Silica gel) work-up of the resulting product mixtures compounds IX (21%) and X (30%) were isolated. Structural assignments of compounds IX and X are based on the following spectral data: IX, nmr($CDCl_3$): 4.10 & 3.55 (AB, J = 10.5 Hz, OCH_2), 2.78 & 2.64 (AB, J = 18 Hz, ring-CH_2), 2.36 (s, $COCH_3$), 1.23 & 0.94 (s, t-butyl). ir(neat): 1704 & 1681 (C=O). ms: 266 (M^+). X, nmr($CDCl_3$): 7.14 (s, vinyl proton), 4.25 & 3.67 (AB, J = 9 Hz, OCH_2), 2.70 (s, CH-CO), 1.97 (sb, OH), 1.45 (s, CH_3), 1.21 & 0.98 (s, t-butyl). ir(KBr): 1701 (C=O). ms: 266 (M^+).

Formation of IX and X can be most rationally explained1) in terms of a coupling reaction between radicals V and VI and hydroxymethyl-radicals generated from solvent methanol according to the equation: $CH_3OH + Bu\dot{O} \longrightarrow \dot{C}H_2OH + BuOH$ to yield VII and VIII, respectively. Subsequent hemiketalization of VIII leads to the observed X. In the case of VII, allylic rearrangement to IX, in which the double bond is in conjugation with the carbonyl groups, seems a reasonable pathway.



Together with the previous results on I, the photochemical behaviour of III suggests an excited intermediate IV which collapses in the indicated way. In methanol solution radical V seems to survive long enough to be trapped by the hydroxymethyl-radical.

Acknowledgment: The computer-simulation work was carried out at University of Zürich, Department of Physical Chemistry by Prof. H. Fischer, to whom we are deeply indebted.

References and Notes

1) H. Lind, H. Loeliger and T. Winkler, J. Polymer Sci., Symposium 57, 225 (1976).

2) J. Lerchova, L. Kotulak, J. Rotschova, J. Pilar and J. Pospisil, J. Polymer Sci., Symposium 57, 229 (1976).

3) H. Lind and H. Loeliger, Tetrahedron Letters 1976, 2569.

4) Irradiation of the n,π^*-transition at 385 nm (ε=233) with a Philips SP 500 high-pressure Hg-lamp and Schott WG 1 (2mm) filter (cutoff at 360 nm), solutions degassed by freeze and thaw cycles.

5) Prepared according to A. F. Bickel and E. C. Kooyman, J. Chem.Soc.(London) 1953, 3211. The product had mp. 70° C and was purified on Silica-gel prior to use.

6) Philips HPK 125 through Pyrex-glass to about 50% conversion.