steric hindrance which have been recognized heretofore.[20]

(20) We gratefully acknowledge support for this research in the form of grants from the Research Corporation and the Petroleum Research Fund, administered by the American Chemical Society. We thank the Wayne State University computing center for making available computing time for the calculations involved.

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Received January 16, 1969

The Spin Resonance Spectrum and Reactivity of the *t*-Butoxy Radical

Sir:

There are several reports in the literature of attempts to observe the esr spectrum of the *t*-butoxy radical (BO·) generated by photolysis of di-*t*-butyl peroxide[1-3] (BOOB) or *t*-butyl hydroperoxide (BOOH).[2-5] Piette and Landgraf[4] irradiated BOOH and observed a one-line spectrum with $g = 2.003$. However, later work indicated that the radical observed was BOO·, rather than BO·,[2,3] and no esr signal was detected on irradiation of carefully purified BOOB.[2] We now find that on irradiation of freshly washed and distilled BOOB, using a high-intensity source and fairly efficient focusing of the light,[6] we observe a one-line spectrum with $g = 2.004 \pm 0.004$. On the other hand, irradiation of 10% BOOH in BOOB produces a radical having a one-line spectrum with $g = 2.015 \pm 0.004$. The latter value is in excellent agreement with the values of 2.014 ± 0.001 for BOO·[3,7] and 2.0146 ± 0.0001 for $\mathrm{C_6H_5C(CH_3)_2OO}$.[8] Irradiation of solid BOOB at −70° produced a radical at $g = 2.004 \pm 0.004$ and a peak to peak width of 12 G.

Using techniques previously described[6] we followed the decay of the signal with $g = 2.004$ at room temperature. The results are reported in Table I. The decay was followed to 60–70% destruction of the radical. The results were plotted according to eq 1. The number of

$$R_0/R = 1 + 2(k_tR_0)t \qquad (1)$$

points in each plot is listed in column 4. The absolute steady-state radical concentration, R_0, in run 1 was determined by double electronic integration using standard pitch as the reference.[6] In runs 2–6 the values of R_0 were determined by comparing the derivative peak heights with that of run 1. The average value thus obtained for k_t is $1.3 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. Several estimates of k_t for BO· have been based upon indirect kinetic studies. Walling and Kurkov have estimated k_t as $1.4 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ in carbon tetrachloride solution by measuring the per cent cage reaction in the decomposition of *t*-butyl hypochlorite and using eq 2 with iodine atom as the standard.[9]

$$k_{t,\mathrm{BO}\cdot} = \frac{a_{\mathrm{BO}\cdot}}{a_{\mathrm{I}\cdot}}\,k_{t,\mathrm{I}\cdot} \qquad (2)$$

$$a = \text{per cent cage reaction}$$

Ingold and Carlsson have arrived at a value of $2.8 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ based on oxidation studies.[10] There is also a report that 10% of the radicals produced in the decomposition of BOOB in isooctane undergo geminate recombination. This would lead to a value of k_t of $10^9\ M^{-1}\ \mathrm{sec}^{-1}$ ($k_t = Ak_\mathrm{D}$, $k_\mathrm{D} \approx 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$). By way of contrast, the observed termination constant for BOO· at 30° can be extrapolated from the data of Maguire and Pink to be $3.0 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$.[2] There are several values of k_t for $\mathrm{C_6H_5C(CH_3)_2OO}\cdot$ in the literature.[8,11,12] The values obtained by esr spectroscopy are $2.2 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ and $3.7 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$, while that obtained from oxidation studies is $0.75 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$.[12] The Russell mechanism for termination of peroxy radicals outlined below shows that the observed rate constant is equal to $k_3k_4/(k_{-3} + k_4)$.[12-14] The vast difference in k_t values

$$2\mathrm{RO_2}\cdot \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{RO_4R} \qquad (3)$$

$$\mathrm{RO_4R} \xrightarrow{k_4} \text{nonradical products} \qquad (4)$$

for BO· and BOO· is due to the fact that $k_{-3} \gg k_4$.[7] When R is benzyl, k_t has been estimated as $1.5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$.[15] This increase is associated with an in-

Table I. Termination Constant for *t*-Butoxy Radical

Run	% destruction	Termination time[a] × 10^3 sec	No. of points	r[b]	Intercept[c]	$kR_0 \times 10^{-3}$ sec^{-1}	$R_0 \times 10^6$ M	$k \times 10^{-9}$ $M^{-1}\ \mathrm{sec}^{-1}$
1	66	2.2	4	0.991	0.94	2.02	1.5± .3	1.4
2	68	2.2	4	0.982	0.83	1.64	1.5	1.1
3	68	2.2	6	0.986	1.02	1.18	1.0	1.2
4	68	2.2	5	0.981	0.78	2.50	2.0	1.3
5	60	5.1	4	0.989	0.94	3.09	2.0	1.5
6	43	2.2	4	0.982	0.97	2.16	1.6	1.4

[a] Time allowed for decay. [b] Correlation coefficient for the least squares line. [c] The intercept should be 1.00.

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crease in k_4 due to a change in termination mechanism as R goes from a tertiary to a primary group.[13,14]

Thus it is clear that k_t for BO· is on the order of 10^9 M^{-1} sec^{-1}, while that for BOO· is about 10^4 M^{-1} sec^{-1}. The value of k_t obtained from direct irradiation of purified BOOB is a strong indication that the species at g = 2.004 is BO·. A g value for this radical would be predicted to be greater than 2.0023 due to the higher spin–orbit coupling constant for oxygen than for carbon.[16] Similarly the g value for BO· should be lower than that of HO· which is reported to be 2.01.[17] Furthermore the lack of hyperfine splitting and the spectral width rule out a radical with the unpaired spin on carbon bearing a hydrogen atom.[18] Certainly the species at g = 2.004 is not BOO·. We are hard pressed to envision a radical produced on irradiation of neat BOOB which is not BO·, BOO·, or a carbon radical with a hydrogen atom attached to the carbon bearing the unpaired spin.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479. We also thank Professor S. I. Chan for stimulating and enlightening discussions on the question of g values and Professor G. A. Russell for pointing out several references.

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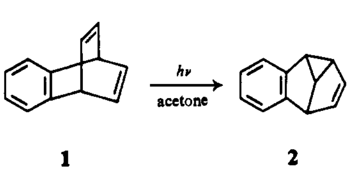
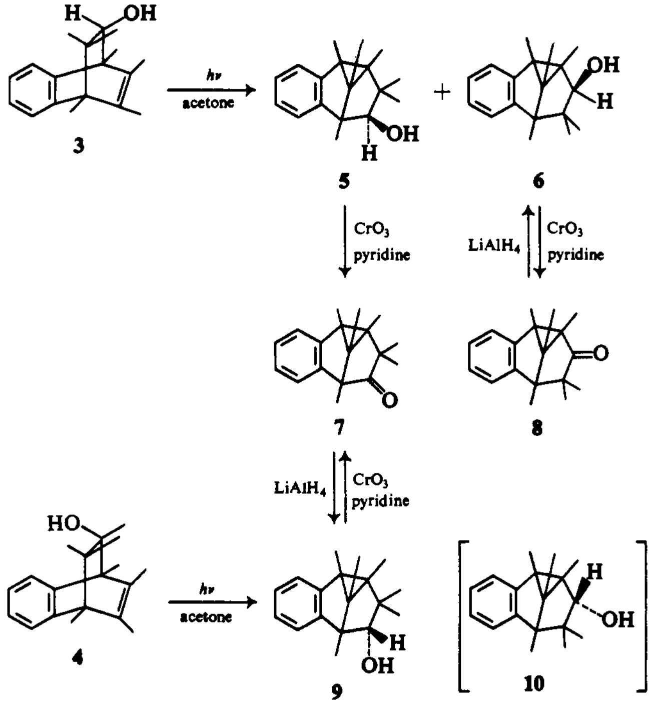
An Unusual Substituent Effect in the Photorearrangement of Benzobicyclo[2.2.2]octadienols

Sir:

Several recent reports[1] have described the photosensitized rearrangement of benzobarrelenes to benzosemibullvalenes. Zimmerman[1a] has shown that the transformation **1** → **2** is the result of vinyl–vinyl, not benzo–vinyl, bridging. However, di-π-methane rearrangements[2] which do involve benzo–vinyl bridging have been observed in the dibenzobarrelene to dibenzosemibullvalene[1b,3] and benzonorbornadiene[4] to tetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene photorearrangements. We have examined the photochemistry of the related epimeric *anti*- and *syn*-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-diene-2-ols (**3** and **4**, respectively) and have found a most unusual substituent effect.



Irradiation of the *anti* alcohol **3**[5] with acetone sensitization through a Corex filter with a Hanovia L 450-W lamp, when allowed to proceed to 85% conversion, provided a 73% yield of a 3:2 mixture of two alcohols, **5** and **6**.[6] Alcohol **5**, mp 81–83°, shows in the infrared[7] a band at 3638 cm^{-1}, and its nmr spectrum consists of three-proton singlets at τ 9.88, 9.03, 8.95, 8.83, 8.67, and 8.63, a one-proton singlet at τ 6.78, and an aromatic multiplet, τ 2.94–3.04 (4 H). Oxidation of **5** with CrO_3–pyridine gave ketone **7**: mp 87–88.5°; $\nu_{C=O}^{CCl_4}$ 1725 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 292 mμ (ε 1290) with shoulders at 313 (800), 301 (1230), and 247 mμ (2980); nmr spectrum: three-proton singlets at τ 9.50, 9.00, 8.80, 8.77, 8.58, and 8.50, and an aromatic multiplet, τ 2.92–3.08 (4 H). Alcohol **6**, mp 90–92°, has in the infrared[7] a band at 3642 cm^{-1}, and its nmr spectrum consists of three-proton singlets at τ 9.33, 9.13, 8.90, 8.85, 8.80, and 8.67, a one-proton singlet at τ 7.08, and an aromatic multiplet, τ 2.94–3.20 (4 H). Oxidation of **6** with CrO_3–pyridine yielded ketone **8**: mp 100–102°; $\nu_{C=O}^{CCl_4}$ 1720 cm^{-1}; $\lambda_{max}^{95\%EtOH}$ 278 (ε 1150) and 270 mμ (1370) with a shoulder at 263 mμ (1450); nmr spectrum (CD_3CN): three-proton singlets at τ 9.44, 8.90, 8.74, 8.68, 8.63, and 8.57, and an aromatic multiplet, τ 2.90–3.22



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