Experimental Section

Materials.—**Anthracene** (Aldrich) was recrystallized twice from benzene and then sublimed, mp 215.0–215.5°. **Maleic anhydride** (Fisher) was recrystallized twice from chloroform and sublimed, mp 53.0–53.5°. **Norbornadiene** (Eastman) was refluxed over $LiAlH_4$ and then fractionated, the fraction of bp 89–90° being used. **Tetracyanoethylene** (Aldrich) was recrystallized from dry chlorobenzene and sublimed, mp 198–199° (sealed tube). **9,10-Dimethylanthracene** was prepared according to the method of Phillips and Cason.[14] After two recrystallizations from benzene and sublimation it had mp 182–183°. **1,4-Dioxane** (Matheson Coleman and Bell, scintillation grade) was distilled from $LiAlH_4$, bp 101°. **Chloroform** (Matheson Coleman and Bell, Spectroquality) was dried over anhydrous $CaCl_2$ and distilled, bp 61°. **Chlorobenzene** (Aldrich) was passed through a column of Linde Molecular Sieves, 4A, and fractionated, the fraction boiling at 131° being used. ***o*-Xylene** (Eastman) was passed through a column of molecular sieves, 4A, and fractionated, the fraction distilling at 143° being used.

Heats of Solution.—The calorimeter and the procedure employed have been described previously.[1e]

---

[14] D. D. Phillips and J. Cason, *J. Amer. Chem. Soc.*, **74**, 2934 (1952).

10-Ethoxy-9-phenanthroxyl Radical and Dimer

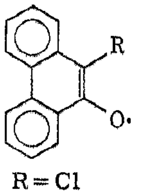
Robert E. Schwerzel and John E. Leffler*

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

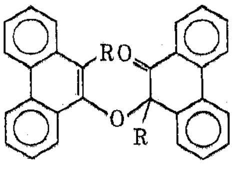
Received April 14, 1972

The dimer of the title radical **1b** is assigned a structure **3** different from that of the dimer **2** of the analogous chloro-substituted radical **1a**. The pmr spectrum of **3** is quite sensitive to temperature effects on the line widths and the epr spectrum of the radical **1b** is affected by solvent as well as by temperature. The spectra of **1a** and **2** are insensitive to solvent and temperature changes. The extent of dissociation of **3** has been measured in several solvents at several temperatures, and is found to increase with increasing solvent internal pressure. The chloro dimer **2** is more than an order of magnitude less dissociated than **3**. The rate constant for the disproportionation of **1b** to 10-ethoxy-9-phenanthrol, phenanthrenequinone, and ethylene is 19 M^{-1} sec^{-1} at 67°.

The dimers of 10-substituted 9-phenanthroxyl radicals, at one time believed to be peroxides, are now known to be keto ethers.[1] In the case of the 10-chloro dimer, the point of attachment of the ether linkage is at the 10 position, as shown in structure 2. This structure is supported by chemical evidence (only one of the two chlorine atoms is labile),[1,2] by the infrared spectrum,[1,2] and by the 90-MHz proton magnetic resonance spectrum,[2] which shows only aromatic protons.



1a, R = Cl
b, R = CH_3CH_2O

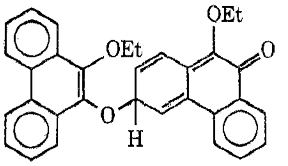


2

The properties of the 10-ethoxy-9-phenanthroxyl radical **1b** and its dimer were different enough from those of the chloro radical and dimer to warrant further investigation. Thus the ethoxy dimer is more dissociated and the line widths of its proton magnetic resonance spectrum are strongly temperature dependent, unlike those of the chloro dimer. Although the latter phenomenon proved not to be suitable for the measurement of dissociation rates[3] in this case, the equilibrium constant for the dissociation has been determined in a series of solvents by means of epr. The decomposition of **1b** into 10-ethoxy-9-phenanthrol, phenanthrenequinone, and ethylene was also studied.

Results and Discussion

Structure of the Ethoxy Dimer.—Although the infrared spectrum of the dimer of **1b** is that of a keto ether, the 90-MHz pmr spectrum has peaks in the vinyl region (doublet at δ 6.4, distorted triplet at δ 7.0), indicating a keto ether structure different from that of **2**. On the basis of the position of the uv absorption maximum (340 nm in CCl_4, ε 4.10×10^3) **3** appears to be the most probable structure.[4]



3

The Temperature-Dependent Pmr Spectrum.—The 90-MHz proton magnetic resonance spectrum of the ethoxy dimer in $CDCl_3$ solution at 0, 25, and 40° is shown in Figure 1. The line broadening and narrowing effects shown in the figure are reversible, although samples heated for extended periods show peaks due to the decomposition product, 10-ethoxy-9-phenanthrol. The small triplet at δ 1.6 is assigned to the latter compound (Figure 1). Complete resolution of the spectrum for quantitative line width studies of the rate of dissociation is prevented by the presence of extra sets of peaks assigned to different conformers of the dimer.[5] These include three different and only partly resolved methyl group triplets centered at δ 0.6, 0.8, and 1.3, and overlapping quartets in the region of δ 2.8–3.7.

---

[1] E. Müller, K. Schurr, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **627**, 132 (1954).

[2] R. E. Schwerzel, Dissertation, Florida State University, 1970.

[3] D. J. Williams and R. Kreilick, *J. Amer. Chem. Soc.*, **90**, 2775 (1968).

[4] Better evidence for **3** was sought by attempting to tautomerize the dimer to the totally aromatic ether by means of acidic and basic catalysts. Unfortunately, the prevailing reaction in all of these experiments was decomposition to phenanthrenequinone, for which polar as well as radical mechanisms can be envisioned.

[5] Molecular models indicate two possible isomeric folded structures for the dimer. Both structures are more compact than an extended structure and might be favored by the internal pressure of the solvent if not by π complexing between the ring systems of the two moieties. In one of the folded structures, each ethoxy group of one moiety is in the shielding region of an aromatic ring of the other moiety; the signal from these groups may be the large triplet at δ 0.6. In the other folded structure, the ethoxy groups are shielded less and to different extents, giving the triplets at δ 0.8 and 1.3.

Epr Spectra and Extent of Dissociation.—Both dimers give multiline epr spectra in degassed 0.10 *M* solution.[2] The spectra are centered about $g = 2.0038$.

The spectrum of **1a**, from the chloro dimer in C_6H_5Cl at 120°, consists of at least 36 apparent lines, most of them showing signs of incipient further resolution. However, the appearance of this spectrum is not noticeably affected by changes either in solvent or temperature, except for its intensity. The width is about 18 G.

The spectrum of **1b**, from the ethoxy dimer, has even more peaks, and in this case additional hyperfine splitting appears at low temperatures and in certain solvents. The width of these spectra is about 16 G. Splittings of about 0.1 G are resolved in tetrahydrofuran (THF) at 23.5°, but not at 52.5°. The spectrum in CCl_4 at 23.5° is also less resolved, resembling that seen in THF at 52.5°.[6]

Extents of dissociation were determined by double integration of overmodulated first-derivative spectra, using galvinoxyl as a standard. The dissociation constants at 25° (by interpolation of van't Hoff plots) are given in Table I. Because of the limited solubility of the chloro dimer, its dissociation constant was determined in only one solvent. The dissociation constant of the ethoxy dimer appears to increase with increasing internal pressure of the solvent, in contrast to that of N_2O_4, which decreases.[7] Solvent effects on the enthalpies and entropies of dissociation are small relative to the experimental error, but both quantities appear to be significantly lower for the chloro dimer than for the ethoxy dimer.

TABLE I

DISSOCIATION EQUILIBRIUM CONSTANTS[a]

Solvent	$10^9\ K_{298}$[b]	$\Delta\bar{H}^0$, kcal/mol, ±2	$\Delta\bar{S}^0$, cal/mol deg, ±7
CCl_4	1.2	21[c]	29
THF	2.9	19[c]	25
C_6H_6	3.3	16[d]	16
$CHCl_3$	4.1	17[c]	19
(C_6H_5Cl)[f]	(0.10)[f]	(8.5)[e,f]	(−17)[f]

[a] The ethoxy dimer **3** unless otherwise noted. [b] Interpolated from the van't Hoff plots. [c] Temperature range, 255–313°K. [d] Temperature range, 293–313°K. [e] Temperature range, 298–392°K. [f] The chloro dimer **2**.

The rate of dissociation of the ethoxy dimer is fast compared with the time of mixing with a radical trapping agent. Thus the dimer is instantly reduced to the phenanthrol by 2,5-di-*tert*-butylhydroquinone. Stopped flow measurements of the rate were not attempted because of overlap of the absorption spectrum of the dimer with that of 2,5-di-*tert*-butyl-1,4-benzoquinone.

The Decomposition of the Ethoxy Dimer 3.—Degassed solutions of the ethoxy dimer slowly decompose to the phenanthrol, phenanthrenequinone, and ethylene, as indicated in eq 1. Phenanthrenequinone has been identified as a product in a previous study.[1] If the product mixture is exposed to air, the yield of phenanthrenequinone is greater than the theoretical value because of oxidation of the phenanthrol.

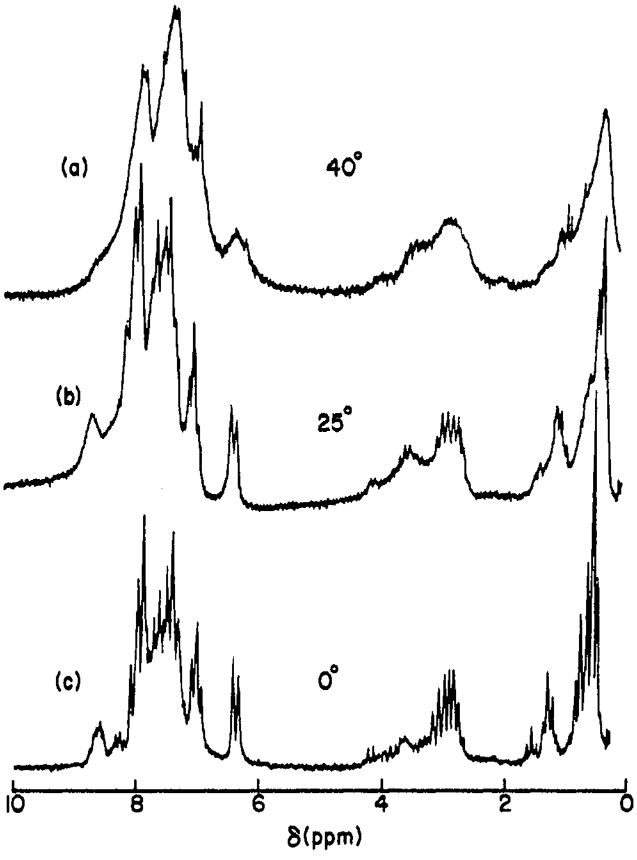
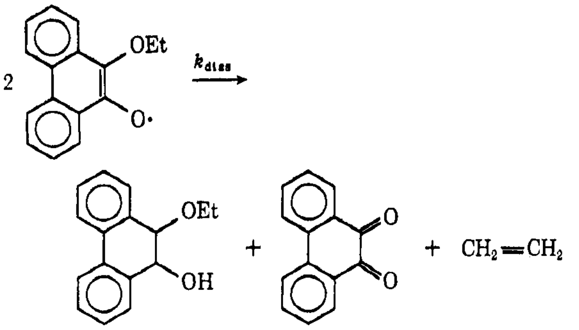


Figure 1.—90-MHz pmr spectrum of the ethoxy dimer in $CDCl_3$.



(1)

Assuming that the dissociation equilibrium is fast and that the mechanism of the decomposition reaction is a disproportionation of the radicals, the rate of disappearance of the radicals will be a first-order process with rate constant $0.5k_{diss}K$. Using the epr signal to monitor the concentration of radicals, $0.5k_{diss}K$ for a 0.02 *M* solution of the dimer in CCl_4 at 67° was found to be 0.65×10^{-6} sec^{-1} and k_{diss} 19 M^{-1} sec^{-1}. A rate constant of about 12 M^{-1} sec^{-1} is estimated for the disproportionation of 2,6-di-*tert*-butyl-4-isopropylphenoxy radicals in cyclohexane at 67°.[8]

---

(6) It is not known what process is responsible for the line broadening and loss of resolution, but we note that the dissociation constant (Table I) is higher in THF than in CCl_4, which may imply a lower recombination rate and less lifetime broadening in THF. A more likely explanation has to do with the rate of intramolecular rotation of the ethoxy substituent. THF has a higher internal pressure than CCl_4, and using a cavity model for the rotation, it should be faster in the latter solvent.

(7) R. J. Ouellette and S. H. Williams, *J. Amer. Chem. Soc.*, **93**, 466 (1971).

(8) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **81**, 1176 (1959).

Experimental Section

10-Chloro-9-phenanthrol and the chloro dimer **2** were prepared by the method of Müller, *et al.*[1]

10-Ethoxy-9-phenanthrol was prepared by a modification of the procedure of Forneau and Matti.[9]

A slurry of 45 g (0.217 mol) of phenanthrenequinone in a mixture of 375 ml of 95% ethanol and 45 ml of H_2O was stirred and heated to reflux. Then, with *vigorous* stirring and refluxing, SO_2 was passed into the reaction mixture for 8 hr, and the dark reddish-brown solution was filtered and cooled to −20° for several hours to crystallize the product. Additional material can be obtained by diluting the filtrate with 10–20 ml of H_2O and cooling overnight at −20°. *It is essential to protect the product from air, as it is very easily oxidized, especially when impurities are present.* It is best purified by several recrystallizations from warm 95% ethanol with rapid cooling to −20°, followed by crystallization from hexane and then again from ethanol. The product is colorless, mp 76–77°. The yield (of pure material) is 8–10 g.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.68; H, 5.88. Found: C, 80.62; H, 5.88.

The ethoxy dimer **3** was prepared using both Müller's procedure[1] and that of Goldschmidt,[10] the properties of the product being the same. Recrystallization from a mixture of chloroform and ethanol gave material melting at 137–138° and with less included solvent of crystallization than recrystallization from the solvent recommended previously.[1,10]

Equilibrium Studies.—All epr spectra were measured in degassed solutions in the same quartz sample tube. The output from the overmodulated first derivative signal was digitized using a Dymec digital voltmeter and a Hewlett-Packard digital recorder. The data were then transferred to punch cards and doubly integrated by means of DINGRT,[11] a program which includes automatic base-line correction after the first integration. The integrated absorptions were then converted to concentrations using a calibration curve based on galvinoxyl.

Registry No.—**3,** 35099-79-7; 10-ethoxy-9-phenanthrol, 35099-80-0.

Acknowledgment.—The authors wish to acknowledge support of this research by the Army Research Office (Durham) and by the National Science Foundation.

---

[9] E. Forneau and J. Matti, *Bull. Soc. Chim. Fr.*, **9**, 633 (1942).

[10] S. Goldschmidt and C. Steigerwald, *Chem. Ber.*, **55**, 3197 (1922).

[11] Supplied by Dr. R. H. Johnsen, Florida State University.

The Induced Decomposition of *tert*-Butyl Peroxide by Ether Radicals. A Nuclear Magnetic Resonance Study

S. H. GOH

Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

Received April 11, 1972

An examination of the products of the decomposition of *tert*-butyl peroxide in 4-chlorobenzyl ethyl ether and 3,4-dichlorobenzyl phenyl ether shows that the formed mixed acetals of the type ArCH(OR)O-*t*-Bu partially decomposed. The formation of the mixed acetal PhCH(OMe)O-*t*-Bu in the decomposition of *tert*-butyl peroxide in benzyl methyl ether was found to be promoted in the presence of added chlorinated solvents. *o*-Dichlorobenzene was found to promote the induced decomposition of the peroxide by several ether radicals; the mixed acetal $CH_3CH(OEt)O$-*t*-Bu was also isolated from a reaction in diethyl ether.

Although for a long time it was commonly believed that *tert*-butyl peroxide is inert to radical-induced decomposition, a property which has made it superior to other organic peroxides, evidence recently obtained indicates that in a number of solvents induced decomposition does in fact occur.[1] In certain primary and secondary alcohols and amines Huyser[2,3] has reported that induced decomposition of the peroxide occurs by hydrogen transfer. In alkyl benzyl ethers $ArCH_2OR$, however, a direct attack of the ether radical on the peroxo linkage has been postulated.[4]

The present paper reports a further study of the reaction products of these systems by nmr spectroscopy and discusses the nature of the induced decomposition reaction.

Results and Discussion

α-Alkoxybenzyl radicals Ar$\dot{C}$HOR, generated by the decomposition of *tert*-butyl peroxide in alkyl benzyl ethers, are known to undergo the following reactions (eq 1–4). Earlier work[1] has shown that for the series

$$2\mathrm{Ar\dot{C}HOR} \longrightarrow (\mathrm{Ar\dot{C}HOR})_2 \qquad (1)$$

$$\mathrm{Ar\dot{C}HOR} \longrightarrow \mathrm{ArCHO} + \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{Ar\dot{C}HOR} + t\text{-}\mathrm{Bu_2O_2} \longrightarrow \mathrm{ArCH(OR)O}\text{-}t\text{-}\mathrm{Bu} + t\text{-}\mathrm{BuO}\cdot \qquad (3)$$

$$\mathrm{Ar\dot{C}HOR} + t\text{-}\mathrm{BuO}\cdot \longrightarrow \mathrm{ArCH(OR)O}\text{-}t\text{-}\mathrm{Bu} \qquad (4)$$

of ethers $PhCH_2OR$ (R = Me, Et, *i*-Pr, *t*-Bu, and Ph) the radical Ph$\dot{C}$HOR only undergoes dimerization and fragmentation reactions (eq 1 and 2). However in chloro substituted benzyl ethers, $ClC_6H_4CH_2OR$ and 3,4-$Cl_2C_6H_3CH_2OR$, kinetic results and the isolation of mixed acetals ArCH(OR)O-*t*-Bu have provided evidence for the induced decomposition and cross-dimerization pathways (eq 3 and 4).[4,5]

4-Chlorobenzyl Ethyl Ether.—In the decomposition of *tert*-butyl peroxide in several alkyl 3,4-dichlorobenzyl ethers it was found that 3,4-dichlorobenzaldehyde was produced in surprisingly high yields (44–88%).[1] Since this is much greater than that expected from simple radical fragmentation (*e.g.*, Ph$\dot{C}$HOMe gives only 10% benzaldehyde), it was suspected that the aldehyde must have originated from another source.

An examination of the reaction products from the decomposition of *tert*-butyl peroxide in 4-chlorobenzyl ethyl ether by nmr spectroscopy revealed that in addition to the expected products, *viz.*, 4-chlorobenzaldehyde, the dimer (4-$ClC_6H_4\dot{C}HOEt)_2$ and the mixed acetal 4-$ClC_6H_4CH(OEt)O$-*t*-Bu, smaller quantities of 4-chlorobenzaldehyde diethyl acetal 4-ClC_6H_4CH-

---

[1] S. H. Goh, R. L. Huang, S. H. Ong, and I. Sieh, *J. Chem. Soc., C*, 2282 (1971).

[2] E. S. Huyser and A. A. Kahl, *Chem. Commun.*, 1238 (1969).

[3] E. S. Huyser, C. J. Bredeweg, and R. M. Vanscoy, *J. Amer. Chem. Soc.*, **86**, 4148 (1964).

[4] R. L. Huang, T.-W. Lee, and S. H. Ong, *J. Chem. Soc., C*, 2522 (1969).

[5] S. H. Goh and S. H. Ong, *J. Chem. Soc., B*, 870 (1970).