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# Peroxides of Sterically Hindered Derivatives of Schlenk Hydrocarbon Diradical

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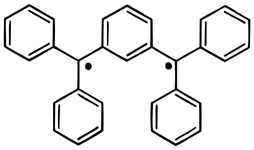
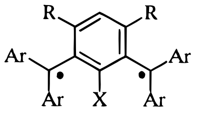
Reaction of oxygen with three sterically hindered derivatives of Schlenk hydrocarbon diradical gives predominantly cyclic peroxides with cross-conjugated $\pi$-systems. For mesitylene-based diradical **3**, significantly different yields of the cyclic peroxide for the reactions in the solid state vs solution were obtained. In the absence of crystallographic studies for Schlenk hydrocarbon and its derivatives, X-ray crystallography for peroxide **1A**-$O_2$ supports the structural assignment for the corresponding diradicals.

## Introduction

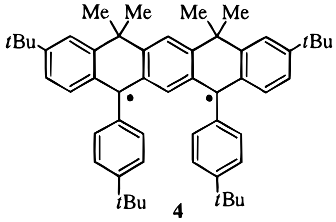
Schlenk hydrocarbon is one of the most famous organic diradicals.[1] It provides an archetype for spin coupling between "unpaired" electrons through the 1,3-phenylene unit—the most ubiquitous spin coupling unit in high-spin di- and polyradicals.[2] Triplet state for Schlenk hydrocarbon was detected by ESR spectroscopy many years ago.[3] Recently, sterically hindered derivatives of Schlenk hydrocarbon,**1-5**, which are stable at ambient temperature, were prepared.[4,5] Their magnetic studies allowed for assignment of the ground states.[2d,4,5]



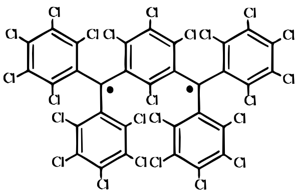
Schlenk hydrocarbon



R = *i*-Pr, X = H, **1**
R = Me, X = H, **2**
R = Me, X = Me, **3**
Ar = 4-*tert*-butylphenyl



**4**



**5**

Important structural evidence for reactive organic radicals and diradicals is typically obtained from analysis of their quenching products.[6−8] Reaction with oxygen, providing peroxides, is one of the most established.[6,7] Reaction of Schlenk hydrocarbon with oxygen was reported by Schlenk and Brauns in their original article, but no products were isolated.[1,9] For other related diradicals, such as the parent *m*-xylylene and its alkyl-substituted derivatives, no corresponding peroxides were reported.[8] Isolation and characterization of peroxides corresponding to derivatives of Schlenk hydrocarbon would not only provide additional evidence for the structure of Schlenk hydrocarbon but also lead to unusual peroxides.

Now we report the characterization of the main products for reaction of diradicals **1**−**3** with $O_2$ in the solid state and in solution (Scheme 1).

## Results and Discussion

Three types of products for the reaction of diradicals **1**−**3** with $O_2$ are considered. These types of products involve formation of C−O bonds at the sites of the expected highest spin density in the diradicals: i.e., triarylmethyl sites and/or *ortho*/*para* positions in the center benzene ring.

Products of type A and B correspond to 1 + 1 condensation of diradical with $O_2$, leading to formation of a 5-membered ring. Product of type C corresponds to 2 + 2 condensation providing a macrocyclic ring; a similar [4.4]metacyclophane ring system, where O−O linkers are replaced with S−S linkers, was prepared by oxidation of the corresponding dithiol under high-dilution conditions (Ar = H and R = H).[10,11]

When solid diradicals **1**−**3** are exposed to air (method I), $^1H$ NMR spectra of the crude mixtures indicate the corresponding peroxides **1A**-$O_2$, **2A**-$O_2$, and **3A**-$O_2$, respectively, as predominant products. **1A**-$O_2$ and **3A**-$O_2$ are isolated in 50-70% yields, but **2A**-$O_2$ could not be obtained in an analytically pure form (Scheme 1).

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1997.

(1) Schlenk, W.; Brauns, M. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 661.

(2) (a) Buchachenko, A. L. *Russ. Chem. Rev.* **1990**, *59*, 307. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88. (c) Iwamura, H. *Adv. Phys. Org. Chem.* **1991**, *26*, 179. (d) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (e) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

(3) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906. Lockhurst, G. R.; Pedulli, G. F. *J. Chem. Soc. B* **1971**, 329.

(4) (a) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, *113*, 9235. (b) Rajca, A.; Utamapanya, S. *J. Org. Chem.* **1992**, *57*, 1760.

(5) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552.

(6) (a) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757; *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3150. (b) Glidewell, C.; Liles, D. C.; Walton, D. J.; Sheldrick, G. M. *Acta Crystallogr. Sect. B* **1979**, *35*, 500. (c) Jang, S.-H.; Gopalan, P.; Jackson, J. E.; Kahr, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 775. (d) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

(7) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165.

(8) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409. Gajewski, J. J.; Paul, G. C.; Chang, M. J.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150.

(9) Stark and co-workers reported their apparently unsuccessful attempts to obtain exocyclic tetraphenyl-substituted *m*-xylylene and its products of reaction with oxygen: Stark, O.; Garben, O. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 659, 2252. Stark, O.; Garben, O.; Klebahn, L. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2542. Stark, O.; Klebahn, L. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 125.

(10) (a) Sato, T.; Wakabayashi, M.; Hata, K.; Kainosho, M. *Tetrahedron* **1971**, *27*, 2737. (b) Dixon, K. R.; Mitchell, R. H. *Can. J. Chem.* **1983**, *61*, 1598. (c) Beveridge, K. A.; Bushnell, G. W.; Mitchell, R. H. *Can. J. Chem.* **1983**, *61*, 1603. (d) Houk, J.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 91.

(11) For a recent collection of reviews on cyclophanes, see: Weber, E., Ed. *Top. Curr. Chem.* **1994**, *172*, 1−201.

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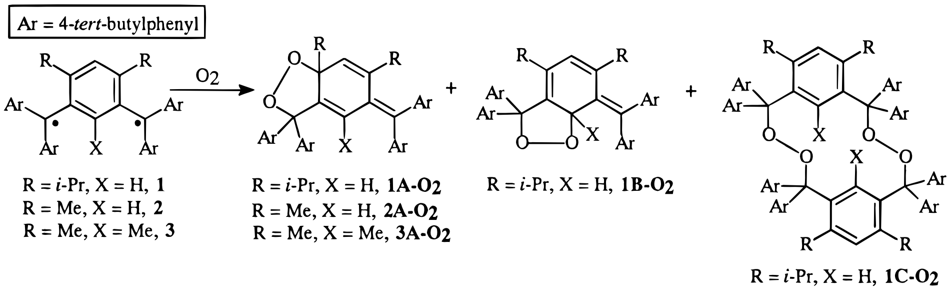
**Scheme 1. Reactions of Diradicals 1−3 with Oxygen**



The spectroscopic evidence for the predominant products, consistent with structure type A or B but excluding type C, is as follows. The $^1$H and $^{13}$C NMR spectra indicate four nonequivalent 4-*tert*-butylphenyl groups, consistent with *cis*/*trans* isomerism with respect to the exocyclic C=C bond and the presence of an stereogenic center. Two nonequivalent *i*-Pr groups, two nonequivalent Me groups, and three nonequivalent Me groups are found in **1A**-$O_2$, **2A**-$O_2$, and **3A**-$O_2$, respectively; furthermore, the methyls of the *i*-Pr groups in **1A**-$O_2$ are diastereotopic. The NMR spectral patterns (chemical shifts) and the expected intense $(M + H)^+$ clusters in FABMS are consistent with all three peroxides having similar structures.

The spectroscopic evidence for the predominant products, indicating that type A is the actual structure, is as follows. In $^1$H NMR spectra, allylic coupling ($J = 1$ Hz) is observed only for one Me group in **2A**-$O_2$ and **3A**-$O_2$, as indicated by the resolved multiplet splittings, and in **3A**-$O_2$, a COSY cross-peak; in **1A**-$O_2$, the allylic coupling gives rise to the ~0.5 Hz splitting of the vinylic resonance and broadening of the corresponding septet of the *i*-Pr group. In $^{13}$C NMR/DEPT spectra for **1A**-$O_2$ and **3A**-$O_2$, the two $^{13}$C resonances in the 80−100 ppm region, which are assigned to the carbons in the peroxide moiety (C−O−O−C), are both detected as quarternary. In FABMS, the most intense clusters in the *m*/*z* 200−1700 range are compatible with the following fragment ions: $(M-C_3H_7)^+$ for **1A**-$O_2$ and $(M-O_2)^+$ for both **2A**-$O_2$ and **3A**-$O_2$.

Structure of **1A**-$O_2$ is confirmed by X-ray crystallography. The C−O−O−C dihedral angle of 26.8° is comparable to the angle of 20° found in a derivative of 1,2-dioxolan.[12] The C-O bond distances (1.47 and 1.46 Å) are essentially identical to those found in triarylmethyl peroxides;[6] the apparent O−O bond distance (1.43 Å) is a few hundredths of an Ångstrom shorter than expected for triarylmethyl peroxide, presumably due to disorder in the crystal of **1A**-$O_2$ (Figure 1).

Analysis of $^1$H NMR spectra for the crude mixtures, obtained by oxidation of solid diradical **1** (method I), reveals three products, with the 100:30:1 relative amounts: (1) a major product **1A**-$O_2$, discussed above, (2) a minor product, and (3) a trace amount of **1C**-$O_2$.[19] The minor product could not be isolated because of its decomposition on silica gel; its $^1$H NMR spectral features, such as two nonequivalent *i*-Pr groups with diastereotopic methyls, four nonequivalent *t*-Bu groups, and two 1-proton resonances in the 5.5−6.5 ppm region, are compatible with structure **1B**-$O_2$, though this evidence does not establish the structure. (These NMR features are analogous to those found in **1A**-$O_2$.)

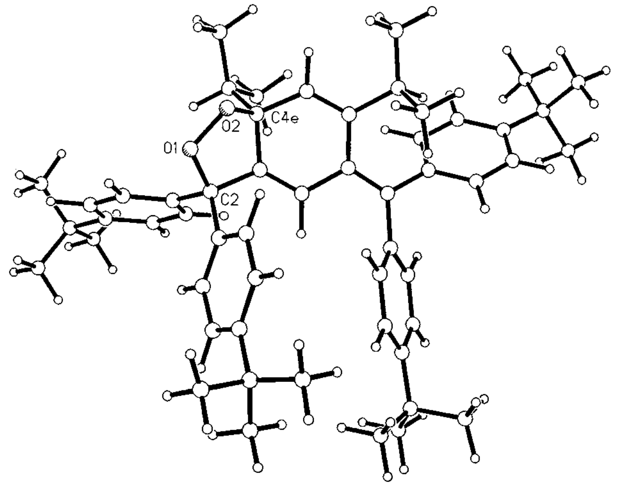


**Figure 1.** Molecular structure and predominant conformation observed for perioxide **1A**-$O_2$ in the solid state. The molecule belongs to point group $C_1$.

Oxidations of diradical **1** in THF at 0 °C, using either pure diradical (method II, Experimental Section) or diradical prepared in situ from dianion (method III, Experimental Section), give **1A**-$O_2$ as a major product. The relative molar amounts of **1A**-$O_2$, tentative **1B**-$O_2$, and **1C**-$O_2$ are 100:(3-6):3; also, there is a small admixture of unidentified products.[19] Notably, **1C**-$O_2$ and the other product, which might tentatively be assigned to **1B**-$O_2$, are formed in significantly greater and smaller yields, respectively, compared to the oxidation in the solid state. Furthermore, oxidations in THF at low temperature (−78 °C) give very complex mixtures, in which only small amounts of **1A**-$O_2$ are detectable.

Spectroscopic evidence for **1C**-$O_2$ is as follows. FABMS gives the expected $(M + H)^+$ cluster centered at $m/z = 1499$ and somewhat less intense fragment ion at $m/z = 1466$, compatible with the loss of $O_2$. Notably, the most intense cluster in the $m/z = 200-1700$ range (ca. 30 times more intense than $(M + H)^+$) is at $m/z = 733.5$, compatible with the loss of $O_2$ and breakage of the other O−O bond. The cluster at $m/z = 705.5$, which is dominant in FABMS for **1A**-$O_2$, has a negligible intensity. $^1$H and $^{13}$C NMR spectra for **1C**-$O_2$ at ambient temperature (~20 °C) contain many broadened resonances. Only one type of *i*-Pr group (with diastereotopic methyls) and two types of *t*-Bu groups are found. Relative integration of the aromatic protons is 1:6:2:3:4:2. The peak with integration of "3" consists of two singlets with different line widths: sharp (integration of "1") and broad (integration of "2"). Two sharp singlets, which have relative integration of "1", have chemical shifts of 9.67 and 6.98 ppm. The $^1$H NMR spectrum at 10 °C is considerably less broadened. In $^1$H NMR spectra at higher temperature (58 °C), all resonances, except for the

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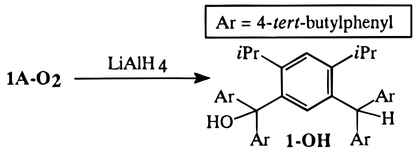
[12] Hitchcock, P. B.; Beheshti, I. *J. Chem. Soc., Perkin Trans. 2* **1979**, 126.

two sharp singlets, assigned to the protons of *i*-Pr-substituted benzene rings in the aromatic region, and the CH protons of the *i*-Pr groups, show even greater broadening.[19] Apparent diastereotopicity is reduced, compared to the spectra at ambient temperature, e.g., methyls of the *t*-Bu groups and *i*-Pr groups appear as broad singlets at 1.3 and 0.5 ppm. Low-temperature structure is compatible with two nonequivalent sets of four 4-*tert*-butylphenyls (e.g., "equatorial" and "axial"); one of the sets shows slow rotation on the $^1$H NMR time scale, presumably due to steric encumbrance by the *i*-Pr groups. At high temperature, both rotation of 4-*tert*-butylphenyls and "equatorial"/"axial" exchange lead to line broadening. The extreme downfield chemical shift (9.67 ppm) for one of the protons at the *i*-Pr-substituted benzene ring may be associated with a particular orientation of the *i*-Pr-substituted benzene ring, analogous to that observed in a [3.3]metacyclophane-based tube-shape molecule;[13] however, additional contributions to shielding/deshielding from both peroxide moieties and benzene rings of 4-*tert*-butylphenyls in many possible conformations of **1C**-$O_2$ may be significant.[10bc,14]

**1C**-$O_2$ is recovered unchanged from treatment with $LiAlH_4$ in THF at ambient temperature; it has been reported that reduction of analogous, but less sterically hindered, peroxide linkage in $Ph_3COOCPh_3$ required reflux in benzene/ether.[15] Reduction of **1A**-$O_2$ with $LiAlH_4$ in ether at ambient temperature gives alcohol **1**-OH; its $^1$H NMR spectra are identical to those reported for **1**-OH, which was prepared via addition of aryllithium to ketone.[16]



When pure diradical **2** in THF at 0 °C is exposed to $O_2$ (method II), **2A**-$O_2$ is the predominant product, analogously to the result obtained for diradical **1**. However, when pure diradical **3** in THF at 0 °C is exposed to $O_2$ (method II), **3A**-$O_2$ is formed and isolated only in small amount. $^1$H NMR spectra of crude mixtures consist of mostly broad unresolved peaks. What is the origin of such drastically different reactivity for **3** in solution vs the solid state? ESR studies suggested that among diradicals **1**−**3**, diradical **3** is the most out-of-plane twisted in frozen 2-MeTHF/THF solutions.[4] Furthermore, in the series of related dianions, charge density in the dianion corresponding to **3** was delocalized to the outer benzene ring to the greatest degree in the series.[4a] The implication is that nonplanarity of the $\pi$-conjugated system of **3** may lead to relatively small spin densities in the center benzene ring, and consequently, formation of cyclic peroxides of types A and B may be less favorable. Thus, it is plausible that conformations of **3** in solution and in the solid state are significantly different.[17] Whether the different conformations of **3** in solution and in the solid state give rise to significantly different strengths of spin coupling (energy gaps between the lowest singlet and triplet states) is an interesting question from the viewpoint of organic magnetism.[18]

## Conclusion

Sterically hindered derivatives of Schlenk hydrocarbon, diradicals **1**−**3**, react with oxygen to form cyclic peroxides **1A**-$O_2$, **2A**-$O_2$, and **3A**-$O_2$ as major products. In the absence of crystallographic studies for Schlenk hydrocarbon and its derivatives, X-ray crystallography for peroxide **1A**-$O_2$ supports structural assignment for the corresponding diradicals.

## Experimental Section.

**General Procedures.** Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone in a nitrogen atmosphere. Major chemicals were obtained from Aldrich. Vacuum line and glovebox techniques are described elsewhere.[16]

NMR spectra were obtained using Omega spectrometers ($^1$H, 500 and 300 MHz) in either $CDCl_3$ or $Me_2SO$-$d_6$; the chemical shift references were as follows: $^1$H, TMS, 0.000 ppm ($CDCl_3$), and $Me_2SO$-$d_5$, 2.490 ppm ($Me_2SO$-$d_6$); $^{13}$C, $CDCl_3$, 77.0 ppm. *J* values are given in hertz. For those selected NMR spectra, where the spectral resolution was digitally improved, the exponent values for exponential multiplication (EM) and Gaussian broadening (GB) are given. IR spectra were obtained using the FT instrument Analect RFX-30 operating in the ATR mode and equipped with a ZnSe ATR plate parallelogram (45°, Wilmad); 2-$cm^{-1}$ resolution was employed.

Elemental analyses were carried out by Dr. G. M. Dabkowski, Director-Microlytics, P.O. Box 199, S. Deerfield, MA 01373.

**X-ray Crystallography 1A-$O_2$.** A single crystal of peroxide **1A**-$O_2$ was obtained as described in the synthetic procedure for reaction of diradicals with $O_2$. Single crystals of $C_{54}H_{68}O_2$ (**1A**-$O_2$) are, at 20 ± 1 °C, triclinic, space group $P\bar{1}$-$C^1_i$ (No. 2) with $a = 11.293(3)$ Å, $b = 11.705(3)$ Å, $c = 19.608(5)$ Å, $\alpha = 108.41(2)°$, $\beta = 96.17(2)°$, $\gamma = 103.70(2)°$, $V = 2342(1)$ Å$^3$, and $Z = 2$ ($d_{calcd} = 1.062$ g·cm$^{-3}$; $\mu_a$(Mo K$\alpha$) = 0.06 mm$^{-1}$). A total of 5392 independent reflections having 2Θ(MoKα) < 43.0° (the equivalent of 0.5 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) $\omega$ scans and graphite-monochromated Mo Kα radiation. The structure was solved using direct methods techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence ($R_1$ (unweighted, based on *F*) =

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(13) Vögtle, F.; Schröder, A.; Karbach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 575.

(14) For an overview of calculations of NMR chemical shifts, with proteins as examples, see: Augspurger, J. D.; Dykstra, C. E. *Prog. NMR Spectrosc.* **1995**, *30*, 1. Ring current contribution: Haigh, C. W.; Mallion, R. B. *Prog. NMR Spectrosc.* **1980**, *13*, 303. Haigh, C. W.; Mallion, R. B. *Org. Magn. Reson.* **1972**, *4*, 203.

(15) $LiAlH_4$ + $(Ph_3CO)_2$: Mustafa, A. *J. Chem. Soc.* **1952**, 2435.

(16) Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **1995**, *117*, 9172.

(17) Two propeller diastereomers could be isolated for the exceedingly hindered perchlorocarbon derivative of the Schlenk hydrocarbon (ref 5).

(18) Whether spin multiplicity will have a significant direct effect on reactivity of **3** toward oxygen is not clear. Recent reports indicate that the rates for the reaction with oxygen are only slightly lower for singlet state diradicals, compared to many triplet state diradicals (with different structures), e.g., Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073. Heath, R. B.; Bush, L. C.; Feng, X.-W.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.* **1993**, *97*, 13355. Furthermore, oxygen and other paramagnetic molecules are known to catalyze intersystem crossing, e.g., Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH: New York, 1995; pp. 254−256. In organometallics, intersystem crossings are expected to be much faster compared to typical organics, but still the notion of significant effect of spin state on reactivity reemerges only to be disproved: Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 11745 and references therein.

(19) See Supporting Information. The author has deposited atomic coordinates for **1A**-$O_2$ with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

0.051 for 3159 independent reflections having $2\Theta(\text{Mo K}\alpha) < 43.0°$ and $I > 3\sigma(I)$ using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all ordered non-hydrogen atoms and isotropic thermal parameters for all included hydrogen atoms. Three of the four *t*-Bu and one of the two *i*-Pr groups are disordered with two preferred orientations for the methyl groups of each in the lattice. The major orientation for each is specified with nonprimed subscripts to the atomic symbols of the methyl carbons and the minor orientation with primed subscripts to the atomic symbols of the methyl carbons. Disordered methyl carbons $C_{12'}$, $C_{13'}$, $C_{14'}$, $C_{32'}$, $C_{33'}$, $C_{34'}$, $C_{42'}$, $C_{43'}$, $C_{44'}$, $C_{52'}$, and $C_{53'}$ were included in the structural model with isotropic thermal parameters; the remaining disordered methyl carbons were included in the structural model with anisotropic thermal parameters.

Before determining the extent of disorder for three of the four *t*-Bu and one of the two *i*-Pr moieties, the 16 methyl groups ($C_{12}$, $C_{13}$, $C_{14}$, $C_{22}$, $C_{23}$, $C_{24}$, $C_{32}$, $C_{33}$, $C_{34}$, $C_{42}$, $C_{43}$, $C_{44}$, $C_{52}$, $C_{53}$, $C_{62}$, $C_{63}$, and their hydrogens) were refined as rigid rotors with $sp^3$-hybridized geometry and a C−H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each methyl group was determined by three rotational parameters. The refined positions for these rigid-rotor methyl groups gave C−C−H bond angles which ranged from 95° to 123°. At that point, a difference Fourier revealed alternate (minor) positions for disordered methyl carbons. These alternate carbon sites were included in the structural model with variable occupancy factors which were normalized over the major and minor sites. Hydrogen atoms were not included in the structural model for minor sites of these disordered methyl groups, and the orientations of the methyl groups for the major sites were no longer allowed to vary in refinement cycles. The following occupancy factors were used for methyl groups in the structural model to describe this disorder: $C_{12}-C_{14}$ and their hydrogens, 0.80; $C_{32}-C_{34}$ and their hydrogens, 0.92; $C_{42}-C_{44}$ and their hydrogens, 0.88; $C_{52}-C_{53}$ and their hydrogens, 0.81; $C_{12'}-C_{14'}$, 0.20; $C_{32'}-C_{34'}$, 0.08; $C_{42'}-C_{44'}$, 0.12; $C_{52'}-C_{53'}$, 0.19. The remaining hydrogen atoms were fixed at idealized $sp^3$- or $sp^2$-hybridized positions using a C−H bond length of 0.96 Å and their isotropic thermal parameters were fixed at values 1.2 times the equivalent isotropic thermal parameter of the carbon atoms to which they are covalently bonded.

**Reaction of diradicals 1−3 with $O_2$.** In all general procedures, described below, crude products were analyzed by $^1$H NMR spectroscopy and TLC; typically, purification by PTLC and further characterization followed. Preparation of diradicals **1**−**3**, corresponding dianions, and diethers was previously described.[4a] Solid diradicals **1**−**3** were stored in a glovebox refrigerator (-30 °C) prior to use.

**Method I:** Solid diradical was loaded into a vial in a glovebox and, then, removed from the glovebox. The diradical was exposed to air for ~1 day. The color of the solid gradually changed from green to yellow.

**Method II:** Solid diradical was loaded into a rubber septum-capped vial or a Schlenk vessel in a glovebox and, then, attached to the nitrogen/vacuum line outside the glovebox. THF was added, and the resultant solution was exposed to dry oxygen at 0 °C. Removal of the solvent in under vacuo gave a crude reaction mixture.

**Method III:** A solution of diradical, which was prepared in situ from the corresponding dianion in THF,[4a] was exposed to dry oxygen at 0 °C. Usual aqueous workup gave a crude reaction mixture.

**Peroxides 1A-$O_2$ and 1C-$O_2$.** All three methods (I−III) gave **1A**-$O_2$ as a predominant product.

**Method III:** Dianion, prepared from the diether (compound **3**-$(OMe)_2$ in ref 4a; 156.7 mg) and Li wire (multimolar excess) in THF (2.5 mL), was oxidized with iodine (51.3 mg).[4a] Exposure of the reaction mixture to dry oxygen gave 157.3 mg of crude product. PTLC (silica gel deactivated with 2% $Et_3N$, 1% ether in hexane) of a 70.0 mg portion of the crude mixture gave two fractions: more polar (46.0 mg, 69%) and less polar (3.3 mg, 5%). The more polar fraction was recrystallized twice from ether/methanol to give 26.0 mg of light yellow crystals, mp 150 °C dec; a single crystal was selected for the structure determination by X-ray crystallography.

The more polar fraction, peroxide **1A**-$O_2$: FABMS (3-NBA) cluster *m/z* (% RA in the *m/z* 200−1700 range) at $(M + H)^+$ 748.5 (10), 749.5 (60), 750.5 (40), 751.5 (10); $(M-C_3H_7)^+$ 704.5 (10), 705.5 (100), 706.5 (70), 707.5 (30); other weak clusters 733.5 (15), 716.5 (25), 689.4 (40); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ ($^1$H-$^1$H COSY cross-peak in the aromatic region) 7.308 (d, $J = 9$, 2 H, 7.080), 7.287 (d, $J \approx 9$, 2 H, 7.14), 7.26 (d, $J$ . 9, overlapped with solvent peak, 2 H, 7.177), 7.194 (d, $J = 9$, 2 H, 7.014), 7.177 (d, $J = 9$, 2 H, 7.26), 7.14 (bd, $J \approx 8$, 2 H, 7.287), 7.080 (d, $J = 9$, 2 H, 7.308), 7.014 (d, $J = 9$, 2 H, 7.194), 6.233 (s, 1 H), 5.883 (d, $J \approx 0.5$, 1 H, EM = −1.5, GB = +0.6), 2.235 (sep, $J = 7$, 1 H), 2.149 (sep, $J = 7$, 1 H), 1.325 (s, 9 H), 1.305 (s, 9 H), 1.297 (s, 9 H), 1.272 (s, 9 H), 1.045 (d, $J = 7$, 3 H), 0.879 (d, $J = 7$, 3 H), 0.851 (d, $J = 7$, 3 H), 0.822 (d, $J = 7$, 3 H); $^1$H NMR (500 MHz, $Me_2SO$-$d_6$): $\delta$ 7.419 (d, $J \approx 9$, 2 H), 7.368 (d, $J \approx 9$, 2 H), 7.326 (d, $J \approx 9$, 2 H), 7.329 (d, $J \approx 9$, 2 H), 7.150 (d, $J \approx 9$, 2 H), 7.104 (d, $J \approx 9$, 2 H), 7.034 (d, $J \approx 9$, 2 H), 6.861 (d, $J \approx 9$, 2 H), 6.029 (s, 1 H), 5.824 (s, 1 H), 2.182 (sep, $J = 7$, 1 H), 2.125 (sep (slightly broadened), $J = 7$, 1 H), 1.278 (s, 9 H), 1.254 (s, 9 H), 1.244 (s, 9 H), 1.205 (s, 9 H), 0.972 (d, $J = 7$, 3 H), 0.832 (bd, $J \approx 7$, 3 H), 0.814 (bd, $J \approx 7$, 3 H), 0.770 (bd, $J = 7$, 3 H); $^{13}C\{^1H\}$ DEPT (135°) NMR (125 MHz, $CDCl_3$); (aromatic/olefinic quaternary region) expected 12 resonances, found 11 resonances at 150.4 (q), 149.9 (q), 149.8 (q), 149.6 (q), 149.4 (q), 142.6 (q), 141.0 (q), 140.3 (q), 139.8 (q), 137.9 (q), 131.7 (q), (aromatic/olefinic nonquaternary region) expected 10 resonances found 10 resonances at 129.1, 128.9, 126.9, 126.6, 125.2, 125.0, 124.94, 124.85, 124.7, 124.6, 120.0, (aliphatic region) 90.7 (q), 89.0 (q), 34.8, 34.55 (q), 34.52 (q), 34.48 (q), 34.37 (q), 31.33, 31.28, 29.5, 24.7, 21.1, 17.3, 17.2; IR ($cm^{-1}$) 2962 (CH), 829 (OO). Anal. Calcd for $C_{54}H_{68}O_2$: C, 86.58; H, 9.15. Found: C, 86.67; H, 9.39.

The less polar fraction, peroxide **1C**-$O_2$: FABMS (3-NBA) cluster *m/z* (% RA in the *m/z* 200−1700 range) at $(M + H)^+$ 1497.0 (40/30), 1498.0 (95/30), 1499.0 (100/30), 1500.0 (70/30), 1501.0 (40/30), calcd for $C_{108}H_{137}O_4$ 1498.05 (80), 1499.06 (100), 1500.06 (60), 1501.06 (25) $(M - O_2)^+$ 1465.0 (70/30), 1466.0 (80/30), 1467.0 (60/30), 1468.0 (35/30), $(M - C_3H_7)^+$ 1455.0 (<20/30), $(M/2)^+$ 747.5 (30), 748.5 (40), 749.5 (70), 750.5 (35), $((M - O_2)/2)^+$ 731.5 (35), 732.5 (95), 733.5 (100), 734.5 (45), $((M/2) - C_3H_7)^+$ 705.4 (<15); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.672 (s, 2 H), 7.119 (d, $J \approx 8$, 12 H), 7.061 (bd, $J \approx 8$, 4 H), 6.978 (s, bs, 6 H), 6.833 (d, $J \approx 8$, 8 H), 6.271 (bd, $J \approx 7$, 4 H), 2.394 (sep, $J = 7$, 4 H), 1.374 (s, 36 H), 1.279 (s, 36 H), 0.516 (bd, $J \approx 6$, 12 H), 0.455 (bd, $J \approx 6$, 12 H), no detectable exchange with $D_2O$; IR ($cm^{-1}$) 2961 (CH), 827 (OO).

**Peroxide 2A-$O_2$.** Methods I and II gave similar results.

**Method II:** Diradical **2** (5.3 mg) in THF (0.5 mL) was exposed to $O_2$ at 0 °C; color of the reaction mixture changed from green to yellow. PTLC (silica gel deactivated with 2% $Et_3N$, 1% ether in hexane) gave 3.4 mg of the product (80+% peroxide **2A**-$O_2$). While peroxide **2A**-$O_2$ was reproducibly obtained in crude mixtures with good yield, its purification was not well reproducible (some PTLC runs gave a fraction of the expected amount); peroxide **2A**-$O_2$ readily decomposed on silica gel (even when pretreated with $Et_3N$ or NaOH): FABMS (ONPOE) cluster *m/z* (% RA in the *m/z* 200−2000 range) at $M^+/(M + H)^+$ 692.5 (10), 693.5 (60), 694.5 (30), 695.5 (<10), $(M - CH_3)^+$ 676.5 (15), 677.5 (45), 678.5 (25), 679.5 (<10), $(M - O_2)^+$ 659.5 (<10), 660.5 (100), 661.5 (65), 662.5 (20); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35−7.20 (m, 10 H), 7.134 (d, $J = 9$, 2 H), 7.054 (bd, $J \approx 9$, 4 H), 6.269 (s, 1 H), 5.877 (d, $J = 1$, 1 H), 1.419 (bs, 3 H), 1.385 (bd, $J \approx 1$, 3 H), 1.319 (s, 9 H), 1.306 (s, 18 H), 1.293 (s, 9 H).

**Peroxide 3A-$O_2$. Method I:** Solid diradical **3** (82.5 mg, 0.122 mmol) was exposed to air for 2 days. Part of the crude product (80.0 mg) was purified by PTLC (silica gel deactivated with 1% NaOH in 93% $EtOH/H_2O$ followed by activation at ~160 °C for 2 days; elution with 5% ether in hexane) to give 52.0 mg (65%) of peroxide. A sample of analytical purity was obtained by recrystallization from ether/MeOH (white solid): FABMS (3-NBA) cluster *m/z* (% RA in the *m/z* 200−1700 range) at $M^+/(M + H)^+$ 705.4 (20), 706.4 (20), 707.4 (45), 708.4

(25), 709.4 (5); $(M - CH_3)^+$ 689.4 (15), 690.4 (25), 691.4 (40), 692.4 (20), 693.4 (10), $(M - O_2)^+$ 673.4 (15), 674.4 (100), 675.4 (70), 676.4 (25); $^1H$ NMR (500 MHz, EM = −1.0, GB = +0.65, $CDCl_3$) $\delta$ ($^1H-^1H$ COSY cross-peak) 7.401 (d, $J = 9$, 2 H, 7.329), 7.329 (d, $J = 9$, 2 H, 7.401), 7.315 (d, $J = 9$, 2 H, 7.249), 7.314 (d, $J = 9$, 2 H, 7.178), 7.249 (d, $J = 9$, 2 H, 7.315), 7.200 (d, $J = 9$, 2 H, 7.151), 7.178 (bd, $J \approx 9$, 2 H, 7.314), 7.151 (d, $J = 9$, 2 H, 7.200), 5.967 (d, $J = 1$, 1 H, 1.365), 1.542 (bs, 3 H), 1.371 (s, 9 H), 1.365 (d, $J = 1$, 3 H, 5.967), 1.298 (s, 9 H), 1.296 (s, 9 H), 1.246 (s, 9 H), 0.889 (s, 3 H). $^1H$ NMR (500 MHz $Me_2SO$-$d_6$) $\delta$ 7.463 (d, $J = 9$, 2 H), 7.364 (d, $J = 9$, 4 H), 7.272 (d, $J = 9$, 2 H), 7.215 (d, $J = 9$, 2 H), 7.198 (d, $J = 9$, 4 H), 7.065 (d, $J = 9$, 2 H), 5.955 (d, $J = 1$, 1 H), 1.518 (s, 3 H), 1.317 (s, 9 H), 1.301 (d, $J = 1$, 3 H), 1.254 (s, 9 H), 1.239 (s, 9 H), 1.218 (s, 9 H), 0.794 (s, 3 H); $^{13}C\{^1H\}$ DEPT (135°) NMR (125 MHz, $CDCl_3$); (aromatic/olefinic quaternary region) expected 13 resonances, found 12 resonances at 151.5 (q), 151.0 (q), 150.4 (q), 150.2 (q), 149.9 (q), 140.8 (q), 140.24 (q), 140.16 (q), 139.7 (q), 138. 4 (q), 137.8 (q), 136.2 (q), (aromatic/olefinic nonquaternary region), expected 9 resonances, found 9 resonances at 129.2, 128.5, 128.4, 128.3, 128.0, 125.1, 124.9, 124.8, 124.4, (aliphatic region) 91.8 (q), 84.9 (q), 34.55 (q), 34.48 (q), 34.39 (q), 31.35, 31.33, 31.37, 22.9, 22.0, 18.0. IR ($cm^{-1}$) 2961 (CH), 824 (OO). Anal. Calcd for $C_{51}H_{62}O_2$: C, 86.64; H, 8.84. Found: C, 86.55; H, 8.75.

**Methods II and III:** $^1H$ NMR and TLC analyses of the crude mixtures revealed a multitude of products and only a low yield of peroxide **3A**-$O_2$. Using method II (21.0 mg of **3** in 1 mL of THF), 1.6 mg (7%) of **3A**-$O_2$ was isolated. In a parallel reaction, using method I (20.4 mg of solid **3**), 11.5 mg (54%) of **3A**-$O_2$ was isolated.

**1-OH (Reaction of 1A-$O_2$ with $LiAlH_4$).** **1A**-$O_2$ (9 mg) was stirred with $LiAlH_4$ (10 mg) in ether (2 mL) for 6 h. Following usual aqueous workup, crude product (9 mg) was obtained. $^1H$ NMR spectrum indicated **1**-OH as predominant product (>80%). PTLC (silica gel deactivated with 2% $Et_3N$, 3% ether in hexane) gave pure product as a white solid (5 mg): FABMS (ONPOE) cluster *m/z* (% RA in the *m/z* 500-1000 range) at $(M - OH)^+$ 717.5 (100), 718.5 (60), 719.5 (20), calcd for $C_{54}H_{69}$ 717.5 (100), 718.5 (62), 719.5 (19); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.23 (d, $J = 8$, 4 H), 7.22 (s, 1 H), 7.17 (d, $J = 8$, 4 H), 7.03 (d, $J = 8$, 4 H), 6.81 (d, $J = 8$, 4 H), 6.43 (s, 1 H), 5.61 (s, 1 H), 3.28 (sep, $J = 7$, 1 H), 3.16 (sep, $J = 7$, 1 H), 2.79 (s, 1 H), 1.29 (s, 18 H), 1.28 (s, 18 H), 1.16 (d, $J = 7$, 6 H), 0.89 (d, $J = 7$, 6 H).

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**Supporting Information Available:** $^1H$ NMR spectra for selected crude reaction mixtures (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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