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(minor) and **11a,d** (major) as thick colorless oils.

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Supplementary Material Available: Data from single-crystal X-ray analyses of the 3,5-dinitrobenzoates esters of **9a** and **11a** (11 pages). Ordering information is given on any current masthead page.

Addition of Oxygen- and Sulfur-Centered Radicals to [1.1.1]Propellane[1]

P. F. McGarry,[2,3] L. J. Johnston,[2] and J. C. Scaiano*[2,3]

Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6, and Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

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There is considerable current interest in the reactivity of molecules with inverted structures at carbon,[4] specially, [1.1.1]propellane.[5] Many processes, such as the additions of *tert*-butyl hypochlorite, thiols, disulfides, diselenides, biacetyl, and halogens are presumed to involve a free-radical mechanism.[6-13] While S_H2 displacements at carbon are extremely rare,[14] reaction at the bridge position in [1.1.1]propellane releases considerable strain and allows both positions with inverted structure to acquire a more favorable conformation. Thus, it is important to obtain absolute rates of radical scavenging by [1.1.1]propellane; we have carried out measurements for *tert*-butoxy and thiophenoxy radicals by use of laser flash photolysis techniques. The results of these studies are reported herein.

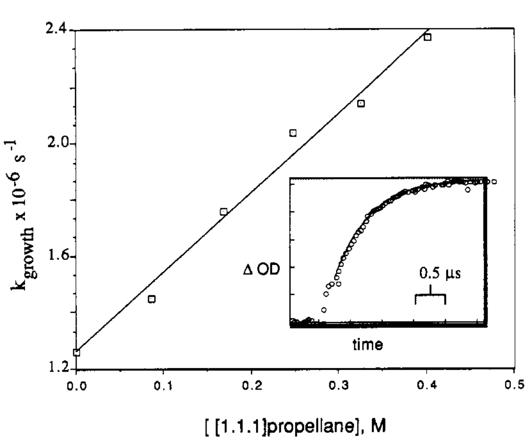


Figure 1. Plot according to eq 5 for [Ph_2CHOH] = 69 mM. Insert: Transient absorption trace showing the buildup of ketyl signal at 535 nm, for 85 mM [1.1.1]propellane.

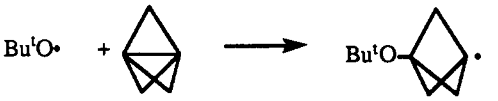
Results and Discussion

tert-Butoxy radicals do not show any significant absorptions at $\lambda > 300$ nm. It was therefore necessary to employ a probe technique that has been widely used in measurements of this type.[15] The radicals were generated by laser photolysis of di-*tert*-butyl peroxide at 337 nm. Reactions 1-4 show the mechanism proposed.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \qquad (1)$$

$$Bu^tO^\bullet \rightarrow \text{first-order decay} \qquad (2)$$

$$Bu^tO^\bullet + Ph_2CHOH \rightarrow Bu^tOH + Ph_2\dot{C}OH \qquad (3)$$



(4)

Reaction 1 generates radicals within the duration of the laser pulse with a high quantum yield.[16,17] The radicals can decay by reacting with the substrate (reaction 4) or the probe (reaction 3, $Ph_2\dot{C}OH$, λ_{max} 535 nm). In addition, $Bu^tO^\bullet$ can undergo first- and pseudo-first-order processes, such as β-cleavage or reaction with the solvent (reaction 2).[15] The buildup of the ketyl signal at 535 nm follows clean first-order kinetics (see insert in Figure 1); a monoexponential fit of the signal growth leads to k_{growth}, which is related to the rate constants of interest according to

$$k_{growth} = k_2 + k_3[Ph_2CHOH] + k_4[\text{propellane}] \qquad (5)$$

Thus, a plot of k_{growth} against the concentration of [1.1.1]propellane at constant diphenylmethanol concentration yields from the slope the value of k_4. The plot of Figure 1 leads to $k_4 = (2.8 \pm 0.3) \times 10^6$ M^{-1} s^{-1} in a 1:1 (v/v) mixture of benzene:di-*tert*-butyl peroxide. This is a remarkably fast reaction, since alkoxy radicals rarely add efficiently to unsaturated systems.[18,19]

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[2] NRCC.

[3] University of Ottawa.

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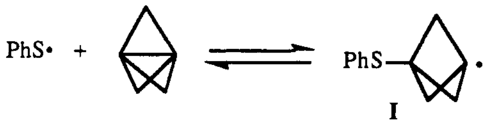
The products of *tert*-butoxy radical addition have been clearly established in the reaction with *tert*-butyl hypochlorite, where the chain reaction leads to addition across the central bond in [1.1.1]propellane.[6] When the alkoxy precursor cannot participate in a chain process—such as the cases of peroxide or *tert*-butyl hyponitrite—we find that the addition of *tert*-butoxy leads to the initiation of [1.1.1]propellane polymerization. The oligomers produced are similar to those already characterized by Michl et al.[11,12] and led to a dramatic increase in solution viscosity in preparative experiments. GC MS data on some of the smaller oligomers suggested that some of them had incorporated the C_4H_9O moiety, as expected.

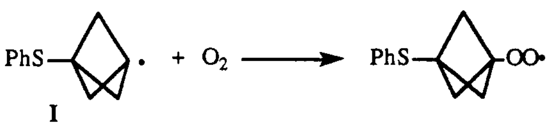
Thiophenoxy radicals, which have a characteristic absorption with λ_{max} at ~440 nm,[20,21] can be readily generated by laser irradiation (308 nm) of diphenyl disulfide. Experiments in deaerated cyclohexane showed that the radicals decay by second-order kinetics, presumably to regenerate the starting material. Addition of [1.1.1]propellane had little or no effect on the rate of thiophenoxy radical decay, despite the fact that studies by Wiberg et al.[6] have clearly shown that this free-radical addition leads to the disulfide addition across the central bond. This situation is not uncommon for reactive radicals and reflects the fact that additions of $PhS^\bullet$ are frequently reversible; Ito and Matsuda[22] have demonstrated that oxygen can be employed to trap carbon-centered radicals produced by reaction of thiophenoxy radicals with styrenes (vide infra) and that under these conditions it is possible to prevent the back reaction. In our case we observe that in the presence of air or oxygen [1.1.1]propellane does quench thiophenoxy radicals and that under these conditions the thiophenoxy radicals decay by pseudo-first-order kinetics; however, the bimolecular rate constant, k_{exptl}, obtained from a plot of k_{decay} vs the propellane concentration is a function of the oxygen concentration (e.g., $(6.4 \pm 0.6) \times 10^6\ M^{-1}\ s^{-1}$ under air), suggesting that oxygen trapping is not quantitative. Reactions 6–9 show the mechanism proposed.

$$PhSSPh \xrightarrow{h\nu} 2PhS^\bullet \quad (6)$$

$$2PhS^\bullet \rightarrow PhSSPh \quad (7)$$



(8)



(9)

Oxygen is known to scavenge quite readily carbon-centered radicals, with rate constants that normally exceed $10^9\ M^{-1}\ s^{-1}$ in fluid solution.[23] In this system oxygen inhibits the regeneration of $PhS^\bullet$, which we suggest occurs via back reaction 8. In principle, the regeneration of $PhS^\bullet$ could have two different origins: (a) reaction 8 may be reversible, as already indicated (by analogy with the case of olefins)[22,24] or (b) radical I may react with the disulfide to yield another $PhS^\bullet$ radical. We believe that (a) is the correct explanation (vide infra). The values of k_{exptl} can be related with the rate constants of interest according to eq 10.

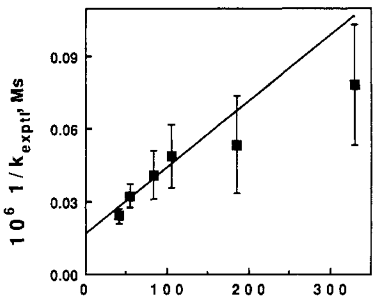


Figure 2. Plot according to eq 10 for the reaction of $PhS^\bullet$ with [1.1.1]propellane. The error bars are based on the dispersion of the data obtained for the decay of $PhS^\bullet$ as a function of [1.1.1]propellane for each oxygen concentration.

$$\frac{1}{k_{exptl}} = \frac{1}{k_8} + \frac{k_{-8}}{k_8 k_9}[O_2]^{-1} \quad (10)$$

Thus, if the oxygen concentration is sufficiently high, the value of k_{exptl} corresponds directly to k_8. Unfortunately, in our case saturation with oxygen in cyclohexane was not sufficient to meet this criterion. In our studies of k_{exptl} vs the reciprocal oxygen concentration, the intercepts of plots according to eq 10 were always too small to allow a meaningful determination of anything other than an upper limit of 5×10^{-8} M s. This establishes a lower limit of $2 \times 10^7\ M^{-1}\ s^{-1}$ for k_8 in cyclohexane. However, in the case of Freon-113 as a solvent (where the oxygen solubility is much higher than in cyclohexane),[25] we were able to obtain significantly better data. Weighted least-squares analysis according to eq 10 (Figure 2) gives an intercept that—in spite of the large error—is significantly different from zero and leads to a k_8 value of $(6.2 \pm 2.0) \times 10^7\ M^{-1}\ s^{-1}$. Combining this with the slope leads to $k_9/k_{-8} \approx 59\ M^{-1}$. Further, examination of reported absolute rate constants for radical reactions with oxygen suggests that the value of k_9 should be in the neighborhood of $4 \times 10^9\ M^{-1}\ s^{-1}$;[23] combining this estimate with the slope from eq 10, we estimate $k_{-8} \approx 6.8 \times 10^7\ s^{-1}$ in Freon-113. This is a remarkably fast rate and may suggest that the addition of $PhS^\bullet$ to propellane is thermoneutral or slightly exothermic. Wiberg and Waddell[7] noted that the adduct of [1.1.1]propellane and PhSSPh can revert back to [1.1.1]propellane by reaction with diaryllithium radical anion.

In spectroscopic studies for both $Bu^tO^\bullet$ and $PhS^\bullet$, we were unable to detect any absorptions due to the corresponding adducts in the spectral window accessible under our experimental conditions ($300 < \lambda < 700$ nm).

In conclusion, alkoxy and thiophenoxy radicals react very rapidly with [1.1.1]propellane, indicating that inverted structures at carbon are highly reactive in addition reactions. For example, in the case of thiophenoxy, our estimated rate constant for addition of $6.2 \times 10^7\ M^{-1}\ s^{-1}$ in Freon-113 indicates that the addition to [1.1.1]propellane is faster than that to styrene, for which we measured a rate constant of $2.2 \times 10^7\ M^{-1}\ s^{-1}$ in cyclohexane. Even radicals

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such as Bu^{t}O$^\bullet$ that do not have a preference for addition reactions, react quite readily with [1.1.1]propellane in an S_H2 type of displacement. In a recent related study, we have demonstrated that diphenylcarbene also adds readily to [1.1.1]propellane with a rate constant of 6.7 × 10^6 M^{-1} s^{-1} to yield a 1,4-biradical.[26]

Experimental Section

[1.1.1]Propellane was prepared following the method of Szeimies et al.[27] and purified by preparative gas chromatography. Di-*tert*-butyl peroxide (MC&B) was passed through an alumina column to eliminate traces of hydroperoxide present as an impurity. Cyclohexane (Aldrich, Spectro grade) was used as received, and Freon-113 (Fluka) was passed through an alumina column to eliminate acid impurities. Diphenyl disulfide (Aldrich) was recrystallized from cyclohexane, and diphenylmethanol (Aldrich) from ethanol. The samples were excited with the pulses from a Lumonics TE860-2 excimer Laser (308 nm, 5 ns, <20 mJ/pulse) in the case of the disulfide and a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, <9 mJ/pulse) for the peroxide. Further details of our laser photolysis system have been reported elsewhere.[28]

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Registry No. Bu^{t}O$^\bullet$, 3141-58-0; PhS$^\bullet$, 4985-62-0; propellane, 35634-10-7.

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5,10,15,20-Tetrakis(α,α,α,α-*o*-(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin: Synthesis and Redox Properties of Zinc(II) and Copper(II) Complexes

Leonin Leondiadis and Michel Momenteau*

Institut Curie, Section de Biologie, Unité Inserm No. 219, Centre Universitaire, Bât. 112, 91405 Orsay, France

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In metalloporphyrins, various chemical and steric factors, such as the substitution of the macrocycle and its microenvironment, control the ligand binding or the electronic-state changes of their central ion. Considering this, superstructures covalently linked to the macrocycle have been used to modulate the reactivity of the metallic center, and they have received considerable attention in the past decade.[1] Thus, it has been reported that the location of secondary amide groups (PhNHCO) in "picket fence" and "basket handle" porphyrins, in the vicinity of the metallic ion, induces unusual behavior in redox and coordination chemistry. This includes stabilization of dioxygen and negatively charged species, due to either hydrogen bonds or dipole–dipole interactions, as well as multiple-electron transfer.[2,3]

To obtain a deeper insight into the effects of the environmental chemical factors, we synthesized 5,10,15,20-tetrakis(α,α,α,α-*o*-(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin (**1**). It was expected that the main consequence of the presence of the "reversed" amide groups (PhCONH) would be the stabilization of positively charged species compared to that observed with Collman's "picket fence" porphyrin (TpivPP,[4] Scheme I).

The key intermediate to the porphyrin **1** was the tetrakis(*o*-carboxyphenyl)porphyrin (**3**). Initial attempts to obtain the latter from *o*-carboxybenzaldehyde failed due to the existence of an intramolecular equilibrium with the 3-hydroxyphthalimide form. On the other hand, condensation of *o*-carbomethoxybenzaldehyde with pyrrole, following Rothemund's method,[5] gave porphryin **5** with a weak yield (2%). The successful approach to obtain porphyrin **3** (Scheme II) involves the preparation of 5,10,15,20-tetrakis(*o*-cyanophenyl)porphyrin (**2**) from the cyclization of *o*-cyanobenzaldehyde with pyrrole, following the same method (11%). On treatment with H_2SO_4 in acetic acid, this tetracyano derivative was hydrolyzed to the desired porphyrin **3**, in a quantitative yield.

Esterification of **3** was accomplished in order to separate the four atropisomers. The tetra-acid chloride **4** was obtained by the use of oxalyl chloride, and it was then quantitatively converted to the tetramethyl ester **5**, with methanol. After α,α,α,α-atropisomer enrichment, under the conditions described by Lindsey,[6] atropisomers were separated by column chromatography on silica gel. The desired α,α,α,α-atropisomer was isolated as the most polar compound, eluted with methylene chloride, in a 32% yield. The identification of the four atropisomers of **5** was also supported by ^{1}H NMR analysis, based on their molecular symmetries (Table I). The spectrum of the α,α,α,α-atropisomer shows a single resonance for the eight pyrrolic protons, confirming their equivalence. The double peak for these protons of the α,α,β,β-atropisomer is explained by the presence of a symmetry plan and a conversion axe, through the pyrrolic nitrogen atoms. The spectrum of the α,α,α,β-atropisomer shows several resonances for the same protons, indicating the absence of symmetry in the molecule. Furthermore the three signals of relative intensity 1,1,2 for the methyl ester protons are in perfect agreement with their statistic distribution on both faces of the macrocycle.

On treatment with basic aqueous ethanol, α,α,α,α-**5** was saponified to tetraacid **3**, which was then converted to the corresponding tetra-acid chloride, as previously. Subsequent final treatment with an excess of *tert*-butylamine afforded the desired 5,10,15,20-tetra(α,α,α,α-*o*-(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin (**1**), in a 56% yield, after purification on preparative silica gel chromatography and crystallization. ^{1}H NMR spectral data ($CDCl_3$) were in complete agreement with the indicated structure (Figure 1). The most significant feature of this spectrum is an upfield shift of methyl protons (at 0.1 ppm) arising from the ring current of the porphyrin ring. The amide protons were observed at 5.4 ppm, a position similar to the chemical shift of the same protons in (*tert*-butylcarbamoyl)phenyl, taken as reference. This shift indicated the absence of ring-current effect on the amide protons, corresponding to their outer position.

Zinc and copper insertion into the porphyrin **1** was accomplished by using zinc(II) and copper(II) chloride, under argon, at 50 °C, in dry tetrahydrofuran, in the presence of 2,6-dimethylpyridine.

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