

Aryl Oxalate Derivatives as Convenient Precursors for Generation of Aryloxyl Radicals

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The use of aryloxy oxalyl chlorides (AOCs), aryloxy oxalyl *tert*-butyl peroxides (AOBs), and diaryl oxalates (DAOs) for unimolecular generation of phenoxy radicals under solution and rigid matrix conditions is described. AOCs are usable for photochemical generation of phenoxy radicals, but are only conveniently stable as precursors when 2,6-di-*tert*-butylated derivatives are used. AOBs may be used as thermal precursors to aryloxyl radicals, since they typically decompose within 2–3 h at 60–85 °C to give phenols. ¹H-NMR solution kinetic studies find that $\Delta H^\ddagger = 31$ kcal/mol, and $\Delta S^\ddagger = +3.4$ cal/mol-K for decomposition of phenoxyoxalyl *tert*-butyl peroxide, consistent with substantial concertedness in peroxide bond cleavage. AOBs and the more stable DAOs are also convenient photochemical phenoxy radical precursors. AOBs yield phenoxy radicals more readily by photolysis than do corresponding DAOs, but the DAOs have fewer side reactions that can quench the product phenoxy radicals.

Introduction

The generation of radicals has been of interest for some time to organic chemists, hence various methods have been developed for doing so. For aryloxyl radicals in particular, a variety of bimolecular generation pathways are well known, but unimolecular generation pathways have not been readily available. In this paper, we describe utilization of aryl oxalate derivatives in thermal and photochemical unimolecular generation of aryloxyl radicals.

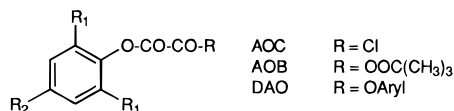
The bimolecular oxidation of phenols to phenoxy radicals in solution has been used extensively in the study of sterically stabilized phenoxy radicals,¹ as well as for generation of transient phenoxy radicals under constant flow conditions.² Typical conditions involve treatment of a phenol in organic solvent with an oxidant such as aqueous basic potassium ferricyanide or solid lead dioxide. The method does not lend itself to use under rigid phase conditions, or where oxidants are undesirable.

An alternative method is photochemical bimolecular oxidation, where a photolabile coreactant is irradiated to form a reactive radical which then abstracts a hydrogen atom from a phenol to give a phenoxy radical. Typical photooxidants of this sort include di-*tert*-butyl peroxide³ and diacetyl.⁴ This methodology eliminates the constant presence of oxidants in radical generation but requires fluid media.

A unimolecular method for generation of fairly stable phenoxy radicals was shown by Cook and Fraser, using symmetric bis-cyclohexadienone peroxides.⁵ This method

works well for clean production of some phenoxy radicals, but is not always synthetically convenient.

As part of our interest in generating aryloxyl radicals in rigid media under conditions where they would have fairly long lifetimes, we needed to develop a general unimolecular methodology. Photolysis of oxalates or carbonates offered obvious choices, though such reactions have not been well-detailed for aryl oxalates or aryl carbonates. For example, solid state radiolysis of diaryl carbonates and polycarbonates has been studied by electron spin resonance (ESR) spectroscopy⁶ and gas evolution⁷ techniques. Radicals have also been generated from alkyl peroxyoxalates and peroxy dicarbonates.⁸ We decided to investigate whether extension of these reactions would allow aryloxyl radical generation.



We found that aryloxy oxalyl chlorides,⁹ aryloxy oxalyl *tert*-butyl peroxy esters,^{9,10} and diaryl oxalates¹⁰ (AOCs, AOBs, and DAOs, respectively) are convenient to synthesize in most cases, and provide the first¹¹ generally applicable photochemical—and in the case of the peroxy esters, thermal—unimolecular sources for aryloxyl radicals. In this contribution, we give full details of our synthetic methodology for these compounds and describe their general characteristics. In addition, we demonstrate some of the variety of uses to which these precursors

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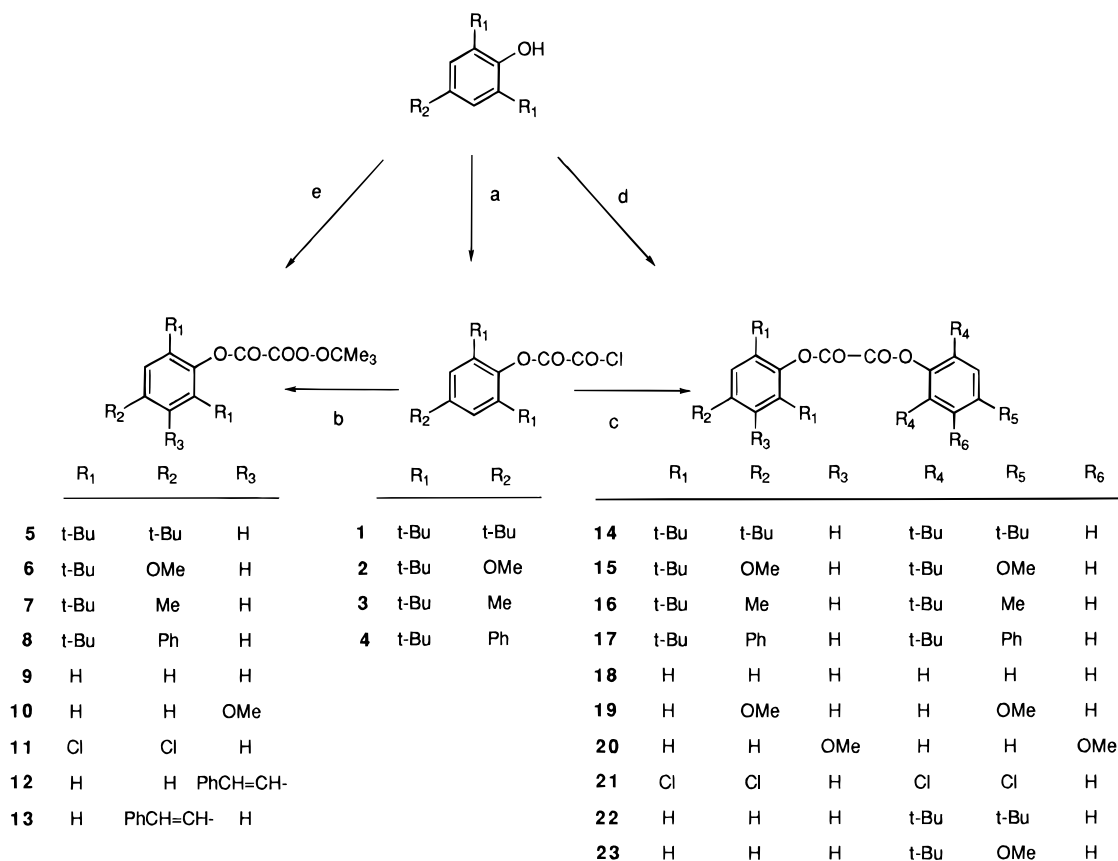


Figure 1. Synthesis of aryl oxalate derivatives used in this study. (a) *n*-BuLi/hexane or NaH/1% EtOH/Et₂O, and then add to excess ClCOCOCl. (b) *tert*-BuOOH/pyridine/Et₂O/0 °C. (c) Add phenoxide solution or suspension generated in a. (d) ArOH/pyridine/0.5 equiv of ClCOCOCl or *n*-BuLi/hexanes/0.5 equiv of ClCOCOCl. (e) *n*-BuLi/hexane or NaH/Et₂O or pyridine/Et₂O, and then add to Me₃COOCOCOCl at 0 °C. Choice of conditions in d and e varies with substitution pattern.

sors may be put in unimolecular aryloxy radical generation. We have not studied in detail each aspect of the thermal and photochemistry of these molecules, but instead concentrate in this paper on demonstrating the broad utility of this approach toward studying aryloxy radical generation in various situations.

Synthesis

Figure 1 summarizes the syntheses of oxalate derivatives **1–23**. The treatment of a phenoxide base with excess oxalyl chloride generates AOCs, which are readily isolable if they bear 2,6-*tert*-butyl substitution, even **2**, whose corresponding AOB could not be isolated⁹ using our methodology.

Treatment of the appropriate AOCs with *tert*-butyl hydroperoxide gives AOBs in most cases. However, efforts to make AOB **6** in this manner instantly yielded a magenta solution even at –40 °C, which was shown by UV–vis and ESR spectroscopy to contain the 2,6-di-*tert*-butyl-4-methoxyphenoxy radical, suggesting that AOB **6** has a low barrier to decomposition, as we will describe further below.

An alternative route to AOBs involves addition of *tert*-butylperoxy oxalyl monochloride (BOC) to the appropriate phenoxide base. This constitutes a general route to making AOBs, with the important caution that *BOC* is an unstable reagent capable of decomposing with considerable vigor under some circumstances. Accordingly, in using BOC we take precautionary measures appropriate for a potentially explosive species, keep the reagent at 0 °C or below at all times, and use the reagent immediately

after generation. We recommend that this material not be stored and that it be made in small quantities. If handled in such a fashion, we find BOC to work quite well to give stable AOBs, including some which proved difficult to make by the route described above. Attempts to make **6** this way, however, again resulted in production of 4-methoxy-2,6-di-*tert*-butylphenoxy radical.

The AOBs tend to be thick oils or low-melting solids. The solids may be substantially purified by low temperature crystallization, but the oils we used without further purification if IR and NMR spectroscopy indicated minimal presence of phenolic impurity. All AOBs synthesized by us decompose upon heating above 50 °C, hence distillation was not deemed feasible. Once isolated, AOBs may be stored in the dark at <0 °C for moderate time periods.

A general route to DAOs is the reaction between a phenoxide base and an AOC shown in Figure 1. Both symmetrical and unsymmetrical DAOs may be synthesized in this way, so long as at least one phenyl ring is 2,6-di-*tert*-butyl substituted. For symmetrical DAOs, addition of 2 equiv of an appropriate phenoxide base to oxalyl chloride yields the DAO. These compounds are much more thermally and photochemically stable than the AOBs and do not suffer from environmental lability like the AOCs. Further details are given in individual sections below.

Results and Discussion

In this section the properties of AOC, AOB, and DAO phenoxy radical precursors are described along with

their use in a variety of phenoxy radical generation experiments. For convenience, the discussion is divided into several subsections, based upon various aspects of the chemistry involved for the derivatives that we studied.

Thermal Decomposition Products and Pathways.

Due to the lability of AOCs and the thermal stability of DAOs, we focused thermal decomposition studies upon AOBs. Direct injection of ethereal solutions of AOBs onto the hot injector (220 °C) of an analytical gas chromatograph showed no production of hydrocarbons, but only of phenols, showing that under these conditions no cleavage of the aryl–oxygen C–O bond occurs to give phenyl radicals.

AOB decomposition was monitored by ¹H-NMR spectroscopy, noting the decrease in the reactant *tert*-butoxy group and concomitant production of *tert*-butyl alcohol and acetone derived by fragmentation of the leaving group *tert*-butoxy radical. Good first-order behavior was noted for decompositions of **9** and **13**, with half-lives at 80 °C of about 2 h. ¹H-NMR kinetic studies in benzene-*d*₆ at 60–85 °C for **9** gave $\Delta H^\ddagger = 31$ kcal/mol, and $\Delta S^\ddagger = +3.4$ cal/mol-deg. For unstable methoxy AOB **6**, if we assume a half-life of 60 s at –40 °C—consistent with our inability to isolate it—use of $A = 10^{13.5}$ yields an activation energy of only 16 kcal/mol.

Since the observed activation enthalpies for decomposition are substantially lower than the homolytic O–O bond dissociation energy of 38 kcal/mol,¹² AOB thermolysis appears to be concerted, rather than stepwise. Peroxides that decompose by rate-determining O–O homolysis are exemplified by *tert*-butyl peracetate,¹³ which has $\Delta H^\ddagger = 38$ kcal/mol and $\Delta S^\ddagger = +17$ cal/mol-deg. *Tert*-butyl phenylperacetate¹³ has $\Delta H^\ddagger = 28.7$ kcal/mol and $\Delta S^\ddagger = +3.9$ cal/mol-deg, consistent with decay by a concerted, two-bond scission pathway leading to the stabilized benzyl radical. Similarly, thermal decomposition of *tert*-butyl phenylpercarbamate¹⁴ has $E_a = 32.5$ kcal/mol. The kinetic parameters for **9** are very similar to those for the latter two decompositions.

The tendency toward concerted decomposition of these species is consistent with the formation of stabilized radical products.^{8,15} If one uses the literature ΔH_f° of the benzyl and phenoxy radicals^{16a} and estimates^{16b} ΔH_f° for *tert*-butyl phenylperacetate and phenoxy *tert*-butylperoxalate **9**, AOB decomposition is as exothermic or somewhat more so than that of a corresponding peracetate. Notably, 4-methoxy substitution decreases the activation barrier to phenylperacetate decomposition¹⁷ by presumed stabilization of a charge-polarized concerted transition state, in qualitative agreement with the strongly acceler-

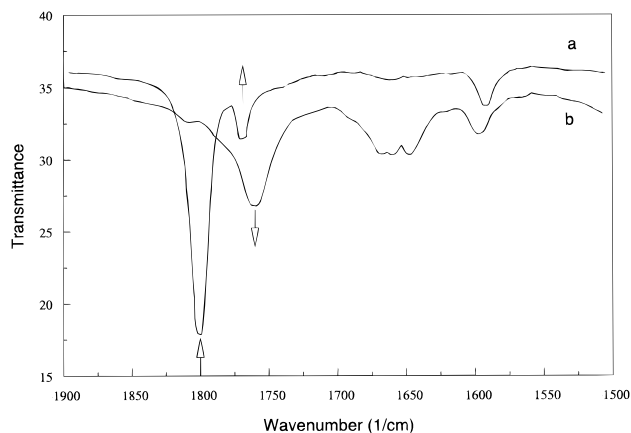
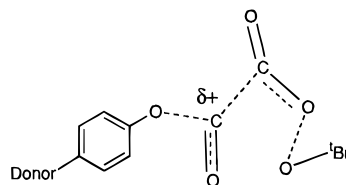


Figure 2. Carbonyl region of Fourier transform infrared spectrum of AOB **5** in KBr matrix before (curve a) and after (curve b) thermolysis at 120 °C for 30 min. Spectra have the same ordinate and abscissa scales. Precursor AOB oxalate peaks (up arrows) and product carbonate carbonyl peak (down arrow) are indicated.

ated decomposition of AOB **6** caused by 4-methoxy substitution on the phenyl ring.



We do not by ¹H-NMR observe products other than phenols and compounds related to the *tert*-butoxy radical when AOB thermolyses are carried out in CDCl₃. But thermolysis of AOB **5** in boiling THF for 4 h yields a small amount of a new carbonyl peak at 1759 cm⁻¹ in the FT-IR spectrum. In rigid KBr matrix at 120 °C, thermolysis of **5** for 30 min yields complete disappearance of the carbonyl peaks associated with the peroxyoxalate moiety (1802 cm⁻¹ and 1769 cm⁻¹, Figure 2), and appearance of a substantial amount of the 1759 cm⁻¹ peak, which we attribute to a carbonate.¹⁸ Recombination of radical fragments may occur within the solvent cage, after initial decomposition of the AOB via a concerted mechanism, paths a or b in Scheme 1. Alternatively, a minor conformer of the AOB may undergo concerted rearrangement and CO₂ extrusion to go directly to the carbonate, path c.

It seems unlikely that carbonate formation would occur via path a, due to the severe entropy and energy penalties incurred over that pathway. Likewise, three-bond scission path a might be expected to have an even more negative ΔS^\ddagger than the +3.4 cal/mol-K that is observed. The similarity of the Eyring parameters for decomposition of **9** to those given above for *tert*-butyl phenylperacetate¹³—which can only undergo two-bond scission in a concerted process—favors the notion that two of the bonds are mostly broken in the transition state for **9**, with the third bond (PhO–CO) being but little affected, as shown in path b. (We thank a referee for stimulating a clarification of the possible three- vs two-bond scission processes in The AOB decompositions.) The PhO–CO radical may have transient existence, consistent with the

(12) For di-*tert*-butyl peroxide $E_a = 37.5$ kcal/mol, $A = 10^{15.8}$ s⁻¹ in Riley, J. H.; Rust, F. F.; Vaughan, W. E. *J. Am. Chem. Soc.* **1948**, *70*, 1336.

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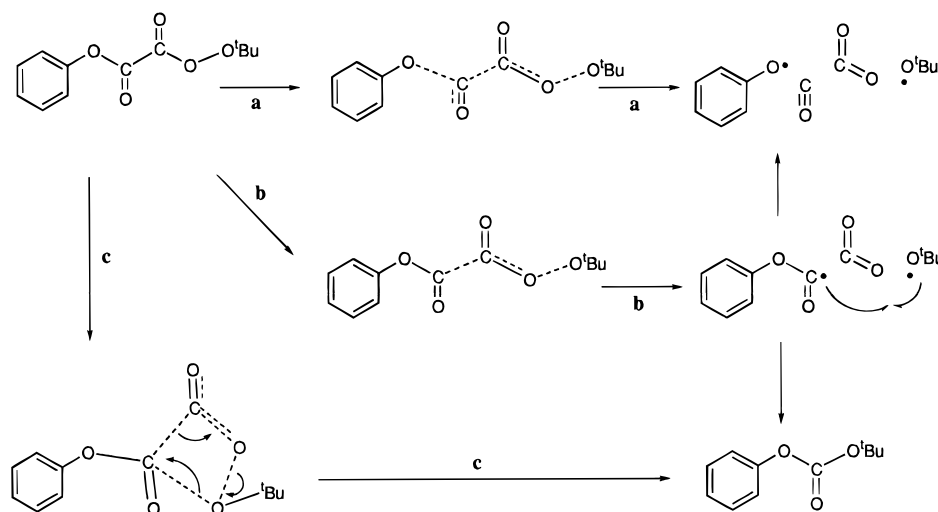
(15) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; p 64ff.

(16) (a) For benzyl radical $\Delta H_f^\circ = 48.0$ kcal/mol, for phenoxy 11.6 kcal/mol, from DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334. (b) Using Stein, S. E.; Rukkers, J. M.; Brown, R. L. NIST Standard Database Program 25, version 1.2 (1991): for *tert*-butyl phenylperacetate and for **9**, estimated ΔH_f° are –78.6 and –139.8 kcal/mol, respectively. Using ΔH_f° for *tert*-butoxy radical, CO₂ and CO of –21.6, –94.1, and –26.4 kcal/mol, respectively, production of phenoxy from **9** is endothermic by about 9 kcal/mol, production of benzyl radical from *tert*-butyl phenylperacetate by about 12 kcal/mol.

(17) Bartlett, P. D.; Hiatt, R. R. *J. Am. Chem. Soc.* **1960**, *82*, 1756.

(18) Ethyl phenyl carbonate has at carbonyl stretch at 1757 cm⁻¹: Hales, J. L.; Jones, J. I.; Kynareon, W. *J. Chem. Soc.* **1957**, 618.

Scheme 1



production of small amounts of carbonate products. Path b thus seems favored by the various evidence. Under the rigid matrix conditions in KBr, intramolecular recombination chemistry becomes more favorable by comparison to solution phase conditions, leading to formation of more carbonate. We shall see that carbonate formation also occurs in photochemical scission of AOBs.

Thermolysis in benzene at 60–85 °C of *tert*-butylated AOBs **5** and **8** for 5 min produces the UV–vis and ESR spectra associated¹⁹ with the expected stable phenoxyl radical products. A quantitative yield of radical is not produced upon decomposition, however. Secondary chemistry destroys the product radicals at elevated temperatures, presumably by return attack of any leaving group radical products upon the phenoxyl radicals, in addition to attack of the phenoxyl radicals on the solvent and upon one another.

By comparison to the AOBs, thermal stability of the DAOs is substantial. For example, diphenyl oxalate **18** readily passes through a gas chromatographic column at 240 °C without observable decomposition to volatile products. A number of other DAOs survive 3 h of heating in boiling tetrahydrofuran, or 1 h of heating at 120 °C in solid KBr, without observable changes to their infrared spectra.

Photolytic Decomposition: Products and Pathways. The UV–vis spectra of AOC, AOB, and DAO oxalate derivatives are fairly similar in the absence of additional conjugating groups, with major absorptions at 240–280 nm and a substantial tail beyond 300 nm that allows photolysis at a slow rate with Pyrex-filtered light. The DAOs have the smallest absorbance beyond 300 nm and photolyze slowly under these conditions.

We did not study photolysis quantum yields for AOCs due to their environmental instability. Relative quantum yields²⁰ for photolysis at 253.7 nm in quartz NMR tubes (acetonitrile-*d*₃ solvent) of 3-methoxy substituted AOB **10** and DAO **20** were measured by monitoring the disappearance of reactant methoxy peaks in the ¹H-NMR spectrum vs appearance of product phenols over the initial 40% of decomposition (Figure 3). Two moles of 3-methoxyphenol were assumed to be produced per mol

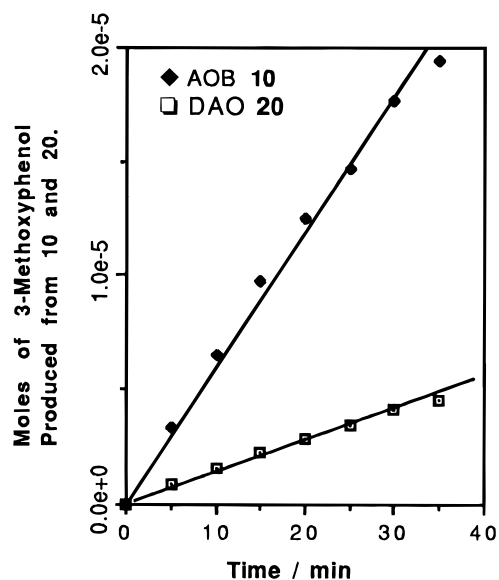


Figure 3. Quantum yield experiments from photolysis at 253.7 nm of AOB **10** (♦) and DAO **20** (□) at room temperature in acetonitrile-*d*₃. Ordinate is moles of product produced, abscissa is minutes of photolysis.

of DAO **20** decomposed. Quantum photolysis efficiencies were 0.42 and 0.11 for **10** and **20**, respectively.

Solution photodecomposition of AOCs, AOBs, and DAOs in hydrogen-atom donor solvents yields only phenols. No aromatic hydrocarbons are observed, indicating minimal production of phenyl radical.²¹ IR spectroscopy shows production of carbon monoxide and carbon dioxide from AOB solution photolysis. ¹H-NMR spectroscopy of AOB photolysates shows production of *tert*-butyl alcohol and acetone derived from the *tert*-butoxy radical leaving group.

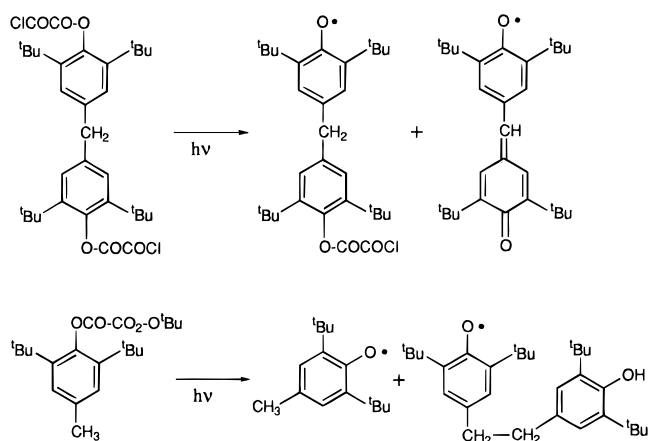
In solution photolysis of AOBs, we find no evidence for reaction of the *tert*-butoxy radical with any aromatic ring products. But, FT-IR analysis of **5** photolyzed in THF

(19) For a summary and leading references, see the review by Altwicker, E. R. *Chem. Rev.* **1967**, *67*, 475.

(20) Hatch, C. G.; Parker, C. A. *Proc. R. Soc. (London), Ser. A* **1956**, *235*, 518.

(21) For phenyl radical, ΔH_f° is 72.5 kcal/mol from Fuji, N.; Asaba, T. *Nippon Kagaku Kaishi* **1977**, *5*, 599. This may be used with the data from footnote 16 to find that production of phenyl radical from **9** has an overall ΔH_f° of about 2 kcal/mol, comparable to the overall enthalpy change for formation of phenoxyl radical. Since this pathway is not observed, the reaction is apparently controlled by preferential breaking of the weakest bonds in **9**, rather than purely thermodynamic factors.

Scheme 2



for 1 h shows a minor amount of a new peak at 1759 cm^{-1} after disappearance of the oxalate peaks at 1800 and 1770 cm^{-1} ; the remainder of the spectrum indicates dominant formation of the expected 2,4,6-tri-*tert*-butylphenol. We attribute the new peak to a carbonate formed in a manner analogously to the carbonate product formed under thermal conditions (Scheme 1).

Photolysis of DAO precursors to 2,6-di-*tert*-butylated phenoxy radicals in tetrahydrofuran or benzene at 253.7 nm quickly leads to production of the colors and UV-vis spectra associated with the anticipated radicals.¹⁸ Though not quantitative, photolytic production of stable radicals from DAOs is more effective than from AOBs, presumably because of fewer and slower side reactions. Fries rearrangement chemistry is possible for the DAOs, but does not appear to occur in solution; a similar lack of rearrangement has been noted for analogous dibenzyl oxalates.²² Product analysis of the photolysates in ethanol of DAOs without *tert*-butyl substitution showed only production of the phenols in modest to good yields.²³ FT-IR analysis of **18** photolyzed in THF shows disappearance of the oxalate carbonyl band at 1765 cm^{-1} within 1 h, with concurrent appearance of the bands expected for 3-methoxyphenol. No new carbonyl bands are observed to indicate formation of a carbonate.

Solution Phase ESR Spectroscopy. AOC photolysis gives useful ESR spectra of phenoxy radicals for cases where AOCs may be isolated, but have not proved very useful in the general case due to their instability. Photolysis of AOBs gives strong radical ESR signals despite the side reactions described earlier, presumably due to their good quantum efficiencies. Both AOCs and AOBs were found in some cases to give ESR active impurities attributable to side reactions (Scheme 2) involving their respective reactive leaving groups, as has also been noted by other groups¹¹ using our methodology. Photolysis of the bis-AOC of bis(4-hydroxy-3,5-di-*tert*-butylphenyl)methane gives a substantial amount of galvinoxyl radical in addition to the expected monoradical product. This is presumably due to abstraction of a methylene hydrogen by a reactive chlorine atom leaving group during photolysis. Photolysis of AOB **7** in benzene leads not only to the ESR spectrum of 2,6-di-*tert*-butyl-4-methylphenoxy radical, but a small amount of an overlapping spectrum (triplet of triplets, $a_1 = 1.6\text{ G}$ and $a_2 = 7.7\text{ G}$) attributable to the dimer caused by abstrac-

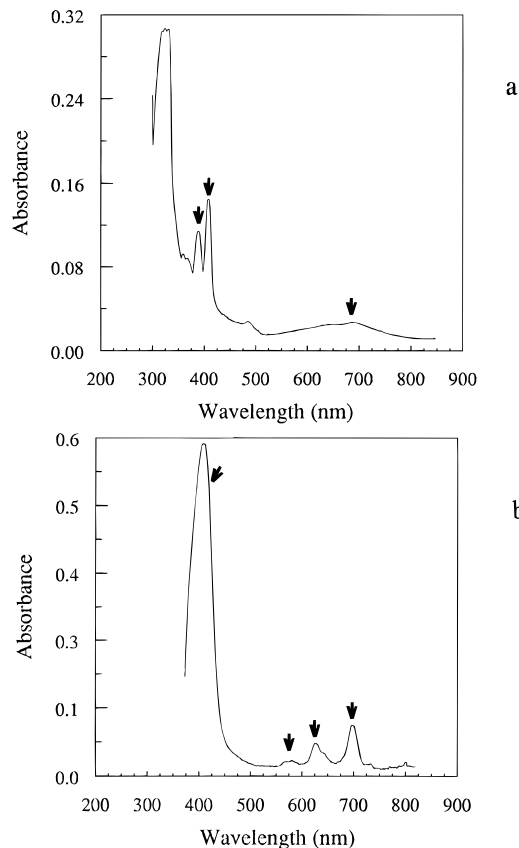


Figure 4. UV-vis spectra from photolyses of AOBs **11** and **13** (spectra a and b, respectively) in polymethylmethacrylate matrices at 77 K . Peaks assigned to product phenoxy radicals are indicated with arrows.

tion of a benzylic hydrogen by the *tert*-butoxyl leaving group, followed by further chemistry (Scheme 2). An analogous product is found²⁴ in photolytic oxidation of 2,6-di-*tert*-butyl-4-methylphenol by di-*tert*-butyl peroxide.

Solution photolysis of *tert*-butylated DAOs gives no ESR spectra other than those attributable to phenoxy radicals. DAOs are thus preferable to AOBs for ESR work if clean production of phenoxy radicals is critical. Overall, we find unimolecular solution photochemical production of stabilized phenoxy radicals to be an effective process, with AOBs being the most photoefficient oxalate precursor, and DAOs being most conducive to phenoxy radical production in the absence of secondary reactions.

Rigid Phase UV-vis and IR Spectroscopy. A major use of these oxalate derivatives is that rigid matrix photochemical generation of phenoxy radicals becomes possible, with suppression of intermolecular chemistry, save for possible recombination of fragments within a matrix cage or quenching by reactive matrices. Photolysis at 77 K of oxalate derivatives in frozen glassy solvents such as 2-methyltetrahydrofuran (MeTHF) or ether/isopentane/alcohol (EPA)—as well as in polymethylmethacrylate (PMMA) and polystyrene (PS) solid films—gives rise to the UV-vis absorbances from the associated phenoxy radicals. Example spectra shown in Figure 4 for the solution-transient 2,4,6-trichlorophenoxy and *p*-stilbeneoxy radicals were obtained in PMMA films at 77 K from AOBs **11** and **13**, respectively. Descriptions of aryloxy radical UV-vis spectra generated by us in

(22) Icli, S.; Nowlan, V. J.; Rahimi, P. M.; Thankachan, C.; Tidwell, T. T. *Can. J. Chem.* **1977**, *55*, 3349.

(23) Horspool, W. M.; Paulson, P. L. *J. Chem. Soc.* **1965**, 5162.

(24) Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2807, 2816.

matrix are given in supporting information. Extinction coefficients were not determined due to lack of knowledge concerning the degree of radical production in the matrices. Our observed spectra agree well with known spectra of phenoxy radicals²⁵ under transient conditions and demonstrate the utility of our unimolecular methodology for rigid phase phenoxy radical generation. At 77 K, the UV-vis spectra appeared to be indefinitely stable after generation, hence our conditions offer substantial advantages in allowing production of phenoxy radicals under conditions where they can be kept for extended times.

Comparison of the thermal persistences of phenoxy radical produced by irradiation of AOB **9** and DAO **18** in PMMA films (monitored by UV-vis spectroscopy at wavelengths > 400 nm) shows the AOB-produced radical to be much depleted²⁶ at temperatures higher than 150 K, while a substantial fraction of radicals remains in the DAO experiment even at temperatures > 220 K. The AOB-produced UV-vis spectra of unstabilized phenoxy radicals fade rapidly at *ca.* 120–170 K in all frozen or solid matrices tested by us. Also, radical decay was observed as the softening temperature was approached in any matrix, regardless of the precursor. AOB photolysis produces a *tert*-butoxy radical held in proximity to the phenoxy radical, and the two may react as the matrix softens. DAO photolysis does not produce such a mobile, reactive leaving group radical, so the fraction of sites conducive to survival of the phenoxy radicals is larger at any given temperature by comparison to an analogous AOB photolysis. However, even stabilized phenoxy radicals produced from DAOs in PMMA films slowly decay. Non-Arrhenius decay behavior is observed for the spectra of radicals from derived from both AOBs and DAOs, consistent with the site specific behavior expected within a matrix.

FT-IR studies in rigid matrix provide some information about one route that decreases the yield of aryloxy radicals from AOBs. Photolysis of AOB **5** in KBr at room temperature with unfiltered xenon arc light for 9 min led to complete disappearance of the carbonyl peaks associated with the peroxyoxalate moiety (1800 and 1770 cm^{-1}), and production of carbon dioxide plus carbon monoxide. In place of these was a substantial new carbonyl peak at 1759 cm^{-1} . The new peak position is identical to that of the carbonate described in the sections on solution thermal and photochemical decomposition of AOBs (Scheme 1). Due to lack of diffusion of radical fragments in the matrix, intramolecular radical recombination may occur to a substantial extent in the solid state at room temperature, in competition with the apparently concerted decomposition that dominates the solution kinetic studies. Carbonate formation may account for part of the disappearance upon warming of phenoxy radicals generated in cryogenic rigid matrices. Alternatively, conformations conducive to direct decarboxylation of AOB to carbonate may be favored in the solid state (Scheme 1, path c).

We do not observe recombination-type products in DAO solid state photolysis of **19**, but only a decrease in the FT-IR spectral intensity of the oxalate moiety. Appar-

ently the propensity for recombination in the solid state is less for DAOs than for the analogous AOBs.

Rigid-Phase ESR Spectroscopy of Phenoxy Radicals. Aryloxy radicals are readily investigated by ESR spectroscopy when generated via oxalate derivative photolysis in neat solid samples, frozen glassy degassed solvents, or cast polymer films. Fluorinated solvents such as Fluorolube give minimal background interference for frozen solution work and are preferred for this use. Related considerations caused us to prefer polymethylmethacrylate to polystyrene for polymer films, since the strong absorbance of polystyrene in the 250 nm region decreased yields of desired phenoxy radicals and gave rise to signals from polystyrene photolysis. When precautions are taken to minimize background radical formation, agreement between the ESR spectral *g*-values of radicals generated by our method and by solution literature methods is good (see supporting information).

The ESR spectra of nonstabilized phenoxy radicals produced in glassy matrices decay irreversibly either upon matrix thawing or in polymer matrices at temperatures above 150 K. ESR spectra of 2,6-di-*tert*-butyl-stabilized radicals produced in polymer matrices persist for days at room temperature under nitrogen when produced from DAO precursors, but decay substantially when the radicals are produced from AOBs, probably as a result of attack by reactive *tert*-butoxy radicals on the phenoxy radicals.

We estimated the radical generation efficiency for AOBs and DAOs by ESR spin counting techniques. PMMA films with known concentrations of AOB **5** and DAO **14** were prepared and cut into portions ~2 mm square by 100 μm thick and weighed, allowing a known number of radical precursor molecules to be used in each experiment. The films were photolyzed at 77 K and the ESR signal intensity obtained, which were compared to the signal intensity of a standard sample of diphenylpicrylhydrazyl radical in PMMA. The reproducibility of results in different experiments implies an even precursor distribution in the films. Control experiments on PMMA show negligible production of radicals from the matrix under our conditions. We defined a 100% spin yield as number of radicals expected for complete photolysis of the radical precursors to phenoxy radicals, when correction is made for the fact that twice as many phenoxy radicals are expected per symmetrical DAO than for an analogous AOB. Little increase in ESR signal intensity occurs beyond 3 h of matrix phase irradiation for either AOBs or DAOs. Under these conditions, the estimated spin yields are 30–40% for AOBs and 20–30% for DAOs.

ESR Spectroscopy of Phenoxy Radical Pairs. In addition to the chemistry of monoradical production described above, we have found that oxalates yield radical pairs upon photolysis. Neat solid state irradiation of various AOBs at 77 K shows only phenoxy radicals in the $g \approx 2$ ($\Delta M_s = 1$) region of the ESR spectrum. But, we have shown that photolysis at 77 K of DAOs **14**, **15**, and **17**^{27a} (among other DAOs^{27b,c}) under the same conditions gives triplet biradical spectra from phenoxy-phenoxy radical pairs, due to cleavage of the DAO to yield two phenoxy radicals held in proximity by the

(25) Cf. the summary on p 482 of ref 19, and Cook, C. D.; Kuhn, D. A.; Fianu, P. J. *J. Am. Chem. Soc.* **1956**, *78*, 2002.

(26) We reported similar behavior of other photochemically generated aryloxy radicals in Modarelli, D. A.; Rossitto, F. C.; Minato, M.; Lahti, P. M. *Mater. Res. Soc. Sympos. Proc.* **1990**, *173*, 83.

(27) (a) Modarelli, D. A.; Lahti, P. M.; George, C. *J. Am. Chem. Soc.* **1991**, *113*, 6329. (b) Modarelli, D. A. Ph. D. Thesis, University of Massachusetts, 1991. (c) Modarelli, D. A.; Kalgutkar, R.; Lahti, P. M. Unpublished results.

rigidity of the crystal lattice. Generation of radical pairs is convenient under the unimolecular matrix generation conditions allowed by DAO precursors and allows the study of exchange interactions between π -radicals generated *in situ* in the solid state, especially if combined with knowledge of the crystallographic nature of the DAOs.²⁸ These studies are ongoing in our group and are further described elsewhere.²⁷

Conclusion

Aryl oxalate derivatives are readily synthesized compounds of wide utility for photochemical generation of aryloxy radicals in fluid or rigid media. A large variety of substitution patterns on these precursors is easily accommodated, resulting in a fairly general unimolecular methodology of aryloxy radical generation. We have found the methodology of applied use for a variety of radical generation needs, and hope to continue to expand the scope of this general strategy in future work.

Experimental Section

***tert*-Butylperoxalyl Chloride (BOC)** (*See caution at the end of this procedure*). In a typical example, oxalyl chloride (6.6 g, 52 mmol) was dissolved in 35 mL of pentane in a 100 mL three-neck round-bottom flask and cooled to 0 °C under nitrogen. A solution of *tert*-butyl hydroperoxide (2.3 g, 26 mmol) in 20 mL of pentane was added slowly over 5 min via an addition funnel and stirred at 0 °C for 30 min. The pentane and excess oxalyl chloride were removed under vacuum, leaving as a residue the oily BOC, which was carefully kept at 0 °C throughout. The vacuum was removed and the system purged with dry nitrogen, at which time 35 mL of anhydrous ether was added. This solution of BOC may be used as described below.

Due to the reactive nature of BOC, caution must be exercised when using this reagent. Care should be taken to keep the compound at a low temperature (~0 °C) at all times, as warming can result in rapid, vigorous decomposition. Only that amount which will be used immediately should be prepared and kept cold, and any unused BOC should be disposed of by addition of *sec*-butyl alcohol with cooling in an ice bath. We recommend not running this reaction on scales significantly larger than those described by us. *Safety precautions appropriate to the potential for vigorous decomposition should always be used with this compound.*

(2,4,6-Tri-*tert*-butylphenoxy)oxalyl Chloride (1). 2,4,6-Tri-*tert*-butylphenol (5.0 g, 19 mmol) was dissolved in 30 mL of anhydrous ether and stirred for 15 min at 0 °C under nitrogen. To this solution was added 12 mL (19 mmol, 1.6 M in hexanes) of *n*-butyllithium in 20 mL of ether, precipitating a white solid. The lithium salt of the phenol was stirred for 5 min before it was poured into a nitrogen-purged 100 mL three-necked round-bottom flask containing 4.8 g (38 mmol) of oxalyl chloride. The solution was stirred for 30 min, and then the solvent and excess oxalyl chloride were evaporated under vacuum at 0 °C. Yellow-white solid **1** was isolated (6.3 g, 94%, 52–54 °C) and was not further purified due to instability. IR (CHCl₃, cm⁻¹): 1801, 1780 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.33 (s, 18 H), 1.45 (s, 9 H), 7.20 (s, 2 H).

(4-Methoxy-2,6-di-*tert*-butylphenoxy)oxalyl Chloride (2). 4-Methoxy-2,6-di-*tert*-butylphenol (2.0 g, 8.5 mmol) was treated by the procedure used for **1** to give product **2** as a white solid (2.0 g, 72%, mp 69–71 °C) which turned oily upon standing and was not further purified due to instability. IR (CHCl₃, cm⁻¹): 1776, 1746 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.26 (s, 18 H), 3.34 (s, 3 H), 6.89 (s, 2 H).

(4-Methyl-2,6-di-*tert*-butylphenoxy)oxalyl Chloride (3). 4-Methyl-2,6-di-*tert*-butylphenol (2.0 g, 9.1 mmol) was treated

by the same procedure used for **1** to give product **3** as an orange oily residue (0.8 g, 45%), which was not further purified due to instability. IR (CHCl₃, cm⁻¹): 1787, 1745 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.25 (s, 18 H), 2.26 (s, 3 H), 6.94 (s, 2 H).

(4-Phenyl-2,6-di-*tert*-butylphenoxy)oxalyl Chloride (4). 4-Phenyl-2,6-di-*tert*-butylphenol (0.50 g, 1.7 mmol) was treated by the same procedure used for **1** to give product **4** was isolated as a yellow oil (0.60 g, 95%), which was not further purified due to instability. IR (CHCl₃, cm⁻¹): 1785, 1760 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.30 (s, 18 H), 7.2–7.7 (m, 7 H).

(2,4,6-Tri-*tert*-butylphenoxy)oxalyl *tert*-Butyl Peroxide (5). AOC **1** (6.3 g, 18 mmol) was dissolved in 50 mL of ether in a 100 mL three-necked round-bottom flask and cooled to 0 °C, and then an ether solution of pyridine (1.5 g, 18 mmol) and *tert*-butyl peroxide (1.6 g, 18 mmol) was added via an equilibrating addition funnel. The reaction mixture was stirred for 15 min at this temperature, before washing with aqueous solutions of 10% H₂SO₄, 10% saturated NaHCO₃, and water and drying over MgSO₄. The ether was evaporated under reduced pressure at 0 °C, to yield white solid **5** which was deemed pure enough by proton NMR to use in experiments (5.53 g, 76%, mp 104–105 °C [quick heating]). IR (KBr, cm⁻¹): 1801, 1769 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.35 (s, 18 H), 1.42 (s, 9 H), 1.46 (s, 9 H), 7.34 (s, 4 H).

(4-Methoxy-2,6-di-*tert*-butylphenoxy)oxalyl *tert*-Butyl Peroxide (6). Various attempts were made to synthesize AOB **6**. BOC was made in the manner previously described, using 3.3 g (26 mmol) of oxalyl chloride and 1.2 g (13 mmol) of *tert*-butyl hydroperoxide. Pentane and excess oxalyl chloride were evaporated under vacuum at 0 °C, after which 35 mL of anhydrous ether was added, and the solution was cooled to 0 °C. In a separate reaction flask, 4-methoxy-2,6-di-*tert*-butylphenol (3.0 g, 13 mmol) was dissolved in dry ether and cooled to -40 °C before *n*-butyllithium (5.0 mL, 13 mmol, 2.5 M in hexane) in 15 mL of ether was slowly added. To the white precipitate that was formed was quickly added the BOC solution at -40 °C. The ESR and UV-vis spectra of the reaction mixture showed the presence of 4-methoxy-2,6-di-*tert*-butylphenoxy radical. Only the starting phenol was isolated after aqueous workup.

(4-Methyl-2,6-di-*tert*-butylphenoxy)oxalyl *tert*-Butyl Peroxide (7). AOC **3** (1.6 g, 5.2 mmol), pyridine (0.43 g, 5.2 mmol), and *tert*-butyl hydroperoxide (0.46 g, 5.2 mmol) were used in the same procedure described for **5** to yield yellow liquid **7** (0.8 g, 45%), which was not further purified. IR (CHCl₃, cm⁻¹): 1795, 1760 (s, C=O); 1159 (C–O stretch). ¹H-NMR (80 MHz, CDCl₃, δ): 1.41 (s, 9 H), 1.21 (s, 18 H), 2.28 (s, 3 H), 6.55–6.96 (m, 2 H).

(4-Phenyl-2,6-di-*tert*-butylphenoxy)oxalyl *tert*-Butyl Peroxide (8). AOC **4** (0.66 g, 1.8 mmol), pyridine (0.15 g, 1.8 mmol), and *tert*-butyl hydroperoxide (0.16 g, 1.7 mmol) were used in the same procedure described for **5** to yield crude **8**, which recrystallized from pentane at -78 °C to give a white crystalline solid (0.17 g, 23%) with mp 103–104 °C. IR (CHCl₃, cm⁻¹): 1760, 1790 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.40 (s, 18 H), 1.42 (s, 9 H), 7.2–7.7 (m, 7 H).

Phenoxyoxalyl *tert*-Butyl Peroxide (9). BOC was made as described above, using 6.6 g (52 mmol) of oxalyl chloride, and 2.3 g (26 mmol) of *tert*-butyl hydroperoxide in 20 mL pentane was added slowly over 5 min via an addition funnel, and stirred at this temperature for 30 min. The pentane and excess oxalyl chloride were removed under vacuum at 0 °C, and the system was purged with dry nitrogen, at which time 35 mL of anhydrous ether was added. A solution of phenol (2.4 g, 25 mmol) and pyridine (2.1 g, 25 mmol) in 15 mL of ether was then slowly syringed in and stirred for 15 min. The reaction mixture was then filtered and washed with aqueous solutions of 10% H₂SO₄, 10% NaHCO₃, and water, before being dried over MgSO₄ and filtered. The ether solution was then placed in a small brown vial, fitted with a septum and the ether evaporated by passing nitrogen through at 0 °C. The remaining solvent was removed by vacuum to give 7.2 g (58%) of colorless oil **9**. Further purification was not attempted due to product instability. IR (neat, cm⁻¹): 1790, 1771 (s, C=O). ¹H-NMR (80 MHz, CDCl₃, δ): 1.43 (s, 9 H); 6.8–7.6 (m, 5 H).

(28) George, C.; Lahti, P. M.; Modarelli, D. A.; Inceli, A. *Acta Crystallogr.* **1994**, *C50*, 1308.

(3-Methoxyphenoxy)oxalyl *tert*-Butyl Peroxide (10). A BOC solution in pentane was made as described above, using 3.79 g of oxalyl chloride (29.8 mmol) and 1.34 g (14.9 mmol) of *tert*-butyl hydroperoxide. A solution of 3-methoxyphenol (0.9 g, 7.5 mmol) and pyridine (1.3 g, 15 mmol) in 15 mL of ether was then slowly syringed in and the reaction stirred for 15 min. The reaction was worked up as described for **9** to give **10** as a clear oil (3.5 g, 57%), which was not further purified. IR (Nujol, cm^{-1}): 1791, 1762 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.42 (s, 9 H), 3.78 (s, 3 H), 6.7–6.9 (m, 4 H).

(2,4,6-Trichlorophenoxy)oxalyl *tert*-Butyl Peroxide (11). A BOC solution in pentane was made as described for **9**, using 10.4 g of oxalyl chloride (81.2 mmol) and 3.66 g (40.6 mmol) of *tert*-butyl hydroperoxide. A solution of 2,4,6-trichlorophenol (4.00 g, 20.3 mmol) and pyridine (1.71 g, 20.3 mmol) in 15 mL of ether was then slowly syringed in and stirred for 15 min. The reaction was worked up as described for **9** to give 18.0 g (64%) of yellow solid **11**, which was not further purified. IR (Nujol, cm^{-1}): 1791, 1762 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.41 (s, 9 H), 7.53 (s, 2 H).

***trans*-3-Stilbenoxyoxalyl *tert*-Butyl Peroxide (12).** BOC was made with oxalyl chloride (0.60 g, 4.7 mmol) and *tert*-butyl hydroperoxide (0.21 g, 2.3 mmol) in pentane as described above. The pentane and excess oxalyl chloride were evaporated under vacuum at 0 °C, and the system was purged with nitrogen, at which time 10 mL of anhydrous ether was added. A solution of 3-hydroxystilbene (0.15 g, 0.75 mmol) and pyridine (0.095 g, 1.1 mmol) in 5 mL of ether was then slowly syringed in and stirred for 15 min. The reaction mixture was then filtered and washed with aqueous solutions of 10% H_2SO_4 , 10% NaHCO_3 , and water, before being dried over MgSO_4 and filtered. The ether solution was then placed in a small brown vial and fitted with a septum, and the ether was evaporated by passing nitrogen over at 0 °C. The remaining solvent was removed by vacuum to give 0.015 g (60%) of clear oil **12**, which was not further purified. IR (neat, cm^{-1}): 1789, 1769 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.43 (s, 9), 6.83–7.03 (m, 2 H), 7.15–7.50 (m, 9 H).

***trans*-4-Stilbenoxyoxalyl *tert*-Butyl Peroxide (13).** BOC was made with oxalyl chloride (1.33 g, 10.5 mmol) and *tert*-butyl hydroperoxide (0.94 g, 10.5 mmol) as described above. A solution of 4-hydroxystilbene (1.50 g, 5.23 mmol) and pyridine (0.44 g, 5.23 mmol) in 5 mL ether was then slowly syringed in and stirred for 15 min. The reaction mixture was then worked up and solvent removed as described for **12** above to yield white solid **13** (0.70 g, 40%, mp 70–71 °C). IR (Nujol, cm^{-1}): 1794, 1771 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.34 (s, 9 H), 7.10–7.55 (m, 11 H).

Bis(2,4,6-tri-*tert*-butylphenyl) Oxalate (14). 2,4,6-Tri-*tert*-butylphenol (7.25 g, 27.6 mmol) was dissolved in 40 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0 °C for 15 min. *n*-Butyllithium (17.8 mL, 27.6 mmol, 1.3 M in hexanes) was added slowly by syringe, precipitating a white solid which was stirred for 10 min, before oxalyl chloride (1.75 g, 13.8 mmol) in 25 mL of ether was added via an equilibrating addition funnel, precipitating a pinkish-white solid. After stirring for 1 h, the ether solution was washed with aqueous solutions of 10% H_2SO_4 , saturated Na_2CO_3 , and water. Drying over MgSO_4 and evaporating the ether under reduced pressure gave 7.30 g of a white powder which was recrystallized from 95% ethanol to yield **14** (4.88 g, 61%, mp 240–241 °C). Anal. Calcd for $\text{C}_{38}\text{H}_{58}\text{O}_4$: C 78.84; H 10.10; O 11.06. Found: C 79.12; H 9.93. IR (Nujol, cm^{-1}): 1755 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.36 (s, 18 H), 1.48 (s, 36 H), 7.45 (s, 4 H).

Bis(2,6-di-*tert*-butyl-4-methoxyphenyl) Oxalate (15). 3,5-Di-*tert*-butyl-4-hydroxyanisole (2.0 g, 8.5 mmol), *n*-butyllithium (3.7 mL, 8.5 mmol, 2.5 M in hexanes), and oxalyl chloride (0.5 g, 4.2 mmol) were used in the same procedure described for **14**. Column chromatography (silica gel, eluent 9:1 *v/v* hexane:chloroform with increasing polarity up to 4:6 hexane:chloroform) and recrystallization of chromatographed product in absolute ethanol at –78 °C yields 0.21 g (9.5%) of **15** as pale yellow prisms, mp 199–202 °C. Anal. Calcd for $\text{C}_{32}\text{H}_{46}\text{O}_6$: C 72.97; H 8.80; O 18.23. Found: C 73.17; H 8.75.

IR (Nujol, cm^{-1}): 1745 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.41 (s, 36 H), 3.78 (s, 6 H), 6.78 (s, 4 H).

Bis(2,6-di-*tert*-butyl-4-methylphenyl) Oxalate (16). To NaH (240 mg, 10 mmol) in 10 mL of dry diethyl ether at 0 °C under nitrogen was added carefully dropwise 4-methyl-2,6-di-*tert*-butylphenol (2.2 g, 10 mmol) in 7 mL of ether. After the resultant white suspension was stirred for 30 min, oxalyl chloride (430 μL , 5 mmol) in 5 mL of ether was added slowly dropwise with the reaction still cooled in an ice bath. The reaction was then stirred at 0 °C for 30 min. The final mix was poured onto ice, washed with 3 N HCl, saturated sodium bicarbonate, and water, and then dried briefly over MgSO_4 . Evaporation under reduced pressure gave a gum, which was recrystallized from pentane at –20 °C to give a pale yellow powder of **16** (830 mg, 17%, mp 129–130 °C). Anal. Calcd for $\text{C}_{32}\text{H}_{46}\text{O}_4$: C 77.69; H 9.37; O 12.94. Found: C 77.41; H 9.19. IR (KBr, cm^{-1}): 1763 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.43 (s, 36 H), 2.24 (s, 6 H), 7.22 (s, 4 H).

Bis(2,6-di-*tert*-butylbiphenyl) Oxalate (17). 3,5-Di-*tert*-butyl-4-hydroxybiphenyl (0.81 g, 2.9 mmol), *n*-butyllithium (1.8 mL, 2.9 mmol, 1.3 M in hexanes), and oxalyl chloride (0.18 g, 1.4 mmol) were used in the same procedure described for **14**. Recrystallization from hexane at –78 °C yielded **17** as a fine white powder (0.11 g, 12%, mp 226–227 °C). Anal. Calcd for $\text{C}_{42}\text{H}_{50}\text{O}_4$: C 81.52; H 8.14; O, 10.34. Found: C 82.07; H 8.29. IR (Nujol, cm^{-1}): 1758 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.44 (s, 36 H), 7.15–7.65 (m, 14 H).

Bis(3-methoxyphenyl) Oxalate (19). Oxalyl chloride (2.5 g, 20 mmol) was dissolved in 25 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0 °C for 15 min. 3-Methoxyphenol (4.9 g, 40 mmol) and pyridine (3.3 g, 40 mmol) in 15 mL of ether were added via an equilibrating addition funnel, precipitating an off-white solid. After stirring for 1 h, the ether solution was washed with aqueous solutions of 10% H_2SO_4 , saturated Na_2CO_3 , and water. The solid was filtered, dissolved in methylene chloride, and dried over MgSO_4 . Evaporation under reduced pressure gave a white powder which was recrystallized from 95% ethanol to give **19** (5.0 g, 83%, mp 145–147 °C). Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_6$: C 63.57; H 4.67; O 31.76. Found: C 63.06; H 4.77. IR (Nujol, cm^{-1}): 1761 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 3.75 (s, 6 H), 6.40–7.12 (m, 6 H).

Bis(4-methoxyphenyl) Oxalate (20). 4-Methoxyphenol (2.0 g, 16.1 mmol), NaH (390 mg, 16 mmol), and oxalyl chloride (700 mL, 8 mmol) were used in the same procedure described for **16**. Dissolution in 1:1 diethyl ether:THF at 40 °C and then cooling to –78 °C yielded **20** as colorless needles (570 mg, 24%, mp 155–156 °C). Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_6$: C 63.57; H 4.67; O, 31.76. Found: C 63.82; H 4.82. IR (KBr, cm^{-1}): 1763 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 3.83 (s, 6 H), 6.80–7.20 (AA'BB' para Ar-H, $J = 11$ Hz, 8 H).

Bis(2,4,6-Trichlorophenyl) Oxalate (21). 2,4,6-Trichlorophenol (6.3 g, 32 mmol), oxalyl chloride (6.3 g, 32 mmol), and 2.5 mL (32 mmol) of pyridine were used in the same procedure described for **19**. Recrystallization from ethyl acetate yielded 3.5 g (50%) of colorless prisms of **21**, mp 186–188 °C. Anal. Calcd for $\text{C}_{14}\text{H}_4\text{O}_4\text{Cl}_6$: C, 37.46; H, 0.90; O, 15.06; Cl, 47.39. Found: C, 37.61; H, 1.05; Cl, 47.17. IR (KBr, cm^{-1}): 1776 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 7.53 (s, 4 H).

2,4,6-Tri-*tert*-butylphenyl Oxalate, Phenyl Ester (22). AOC **1** (1.7 g, 4.9 mmol) was dissolved in 15 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0 °C for 15 min, and then a solution of the phenol (0.38 g, 4.1 mmol) and pyridine (0.34 g, 4.1 mmol) in 30 mL of ether was added over 30 min via an equilibrating addition funnel. The solution was stirred for 30 min more and then washed with aqueous solutions of 10% H_2SO_4 , saturated Na_2CO_3 , and water. Drying over MgSO_4 and evaporating the ether under reduced pressure afforded a brownish-white solid, which was recrystallized from 95% ethanol to yield white rodlike crystals of **22** (0.8 g, 49%, mp 104–105 °C). Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{O}_4$: C 76.06; H 8.35; O 15.59. Found: C 76.29; H 8.49. IR (Nujol, cm^{-1}): 1780, 1751 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.34 (s, 9 H), 1.41 (s, 18 H), 7.20–7.50 (m, 7 H).

2,6-Di-*tert*-butyl-4-methoxyphenyl Oxalate, Phenyl Ester (23). AOC **2** (1.68 g, 7.1 mmol) was dissolved in 15 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0 °C for 15 min, and then a solution of the phenol (0.38 g, 4.1 mmol) and pyridine (0.34 g, 4.06 mmol) in 30 mL of ether was added over 30 min via an equilibrating addition funnel. The solution was stirred for 30 min more and worked up as described for **22**. Column chromatography with chloroform on silica yielded **23** as a yellow oil (1.22 g, 45%). IR (Nujol, cm^{-1}): 1790, 1760 (s, C=O). $^1\text{H-NMR}$ (80 MHz, CDCl_3 , δ): 1.40 (s, 18 H), 3.80 (s, 3 H), 6.80–6.95 (m, 7 H).

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Supporting Information Available: General procedures and syntheses of 3-methoxystilbene, 3-hydroxystilbene, and **18**; procedures for kinetic studies on **9** and **13**; general procedures for cryogenic ESR and UV–vis spectrometry, preparation of oxalate precursor samples in PMMA matrix, ESR spin counting experiments, and actinometry experiments; Tables S1 and S2 of UV–vis absorbance wavelengths and ESR g -values for phenoxy radicals generated from oxalate precursors (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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