Diaryl Oxalates as Convenient Unimolecular Sources of Aryloxyl Radicals

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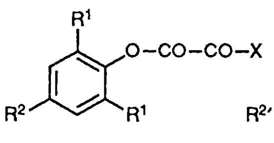
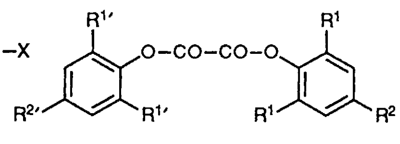
Diaryl oxalates are readily synthesized, stable, convenient unimolecular sources for aryloxyl radicals under solution and rigid-phase photochemical conditions.

Aryloxyl radicals have been and continue to be a subject of substantial interest to chemists, since they are present in a variety of biological, polymeric, and related chemical processes. In addition, recent work has suggested the potential practical use of polyphenoxyl-based polymers in the development of organic magnetic information storage materials.[1,2] In work involving phenoxy systems, generation of the desired radicals has typically involved solution-phase chemistry. The classic studies by Mueller and co-workers[3] of sterically blocked, stabilized phenoxy systems involved solution-phase bimolecular oxidation with various reagents such as lead(IV) oxide, basic aqueous potassium hexacyanoferrate(III), or manganese dioxide; similar chemistry is often used to investigate transiently stable aryloxy systems under continuous-flow conditions. Other methods of generation have employed photochemical hydrogen atom abstraction by a co-reactant in the presence of phenols,[4,5] yielding the desired phenoxyl radical. We recently described[6] the synthesis and use of aryloxyoxalyl t-butyl peroxides and chlorides (**1**) and (**2**), respectively, as convenient unimolecular sources of aryloxyl radicals under solution conditions and in polymeric matrices. A unimolecular thermal method for generating



(1) X = OOBu^t
(2) X = Cl



(3)

phenoxyl radicals from symmetrical bis-4-oxocyclohexadienyl peroxides has been described.[7] In this paper, we report the use of the diaryl oxalates (**3**) (DAO) as unimolecular photochemical sources of phenoxyl radicals, and their superior stability and ease of use compared with our previously reported unimolecular aryloxyl radical sources.

Symmetric 2,6-di-t-butyl substituted compounds (**3**) ($R^1 = R^{1'} = Bu^t$) are readily synthesized by stirring oxalyl chloride with the lithium salt of the corresponding phenol (2 mol equiv.) in diethyl ether at 0 °C. Compounds (**3**) are thermally much more stable than their t-butyl peroxide counterparts (**1**), have been crystalline solids in all cases tested by us to date, and appear in general not to decompose at an appreciable rate below their melting points, whereas compounds (**1**) all decompose at temperatures below 80 °C. The 4-methoxy compound (**1**, $R^1 = Bu^t$, $R^2 = OMe$) cannot be isolated, while the analogue (**3**, $R^1 = R^{1'} = Bu^t$, $R^2 = R^{2'} = OMe$) is readily prepared. Overall, we find that compounds (**2**) are not practically useful phenoxyl radical precursors unless the positions *ortho* to the radical site are t-butylated, and even these have short shelf-lives (less than one month). In contrast, compounds (**3**) are conveniently stored in the dark under nitrogen at ambient temperature, without special efforts to avoid atmospheric water, and appear to be indefinitely stable under these conditions.

Upon irradiation through quartz in benzene solution with either a Rayonet carousel photoreactor (254 nm bulbs) or with a Kratos unfiltered 1000 W Xenon arc, symmetrical 2,6-di-t-butyl-4-substituted compounds (**3**) give rise to the previously described† persistent ESR and UV–VIS spectra typical of the corresponding 2,6-di-t-butyl-4-substituted phenoxyl radicals. No appreciable difference was noted between the stable radical spectra obtained by photolysis of (**3**) and by PbO_2 oxidation of benzene solutions of appropriately substituted phenols. We find by comparative spin-counting ESR experiments that photocleavage of compound (**3**, $R^2 = R^{2'} = Bu^t$) proceeds about half as fast‡ as that of the corresponding compound (**1**), but with two possible radicals per monomer leads to approximately the same yield of radicals per unit time per quantum. Overall, we find that compounds (**3**) are effective solution photochemical radical sources. In addition, their photolysis in rigid media, such as degassed frozen 2-methyltetrahydrofuran or degassed poly(methylmethacrylate) (PMMA) cast films is satisfactory. The PMMA films are particularly convenient as rigid matrices for ESR and UV–VIS spectral samples, and are transparent to the eye up to 10% DAO by weight. Further, most compounds (**3**) we have studied form excellent single crystals (usually long needles), which upon irradiation yield strong ESR spectra. We are presently using these crystals in oriented ESR studies of intermolecular spin–spin interaction of geminate radical pairs in the solid state.

Finally, we have found that synthesis of unsymmetrical compounds (**3**) ($R^n \neq R^{n'}$) is straightforward, if the relatively stable compound (**2**, $R^1 = R^2 = R^3 = Bu^t$) is coupled with various phenols as described earlier. The ESR spectrum of the corresponding 2,4,6-tri-t-butylphenoxyl radical is distinct and relatively narrow (≈12 G wide in solution, about 3—4 times broader in solid matrix; 1 G = 10^{-4} T). As a result, with account being taken of the narrow resonance from this radical as a leaving group, we can generate and detect by ESR spectroscopy radicals with intrinsically broader spectra, such as *p*-stilbenoxyl radical [previously observed from photolysis of the corresponding compound (**1**)[8]] generated at 77 K in a neat powdered solid sample of (**3**) or in a 10% PMMA film. This raises the possibility of using compounds (**3**) as convenient groups for photochemical generation of multiple pendant phenoxyl radical sites on a molecule or polymer chain.

Our findings, taken with our earlier results for compounds (**1**) and (**2**), demonstrate a variety of new unimolecular methods for generation of phenoxyl radicals under solution, rigid-matrix, and oriented-crystal environments. We note that unimolecular methods of phenoxyl radical generation under rigid conditions have not been commonly employed, save for photolysis of some phenols.[9] Given recent interest in synthesizing high-spin organic polyradicals,[1,2] we hope that compounds (**1**) and (**3**) will prove useful in the photochemical generation of organic polyradicals in rigid media as potential information storage materials, as well as in studies of aryloxyl radicals themselves.

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† *Cf.* ref. 6 for ESR and UV–VIS descriptions of phenoxyl radicals prepared from compounds (**1**) and (**2**) which were the same as spectra obtained in the present work.

‡ In hexane solution compounds (**3**) generally decompose completely within 3 h of irradiation in a Rayonet reactor (254 nm bulbs). Although they appear to be photolysed more slowly than the corresponding compounds (**1**), the yield of stable radicals is better. Possible competing photoprocesses are under investigation, but pathways that decrease yields of product radicals appear to involve radical dimerization or reaction with solvents, depending upon substitution.