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CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS
I – ARYLOXYOXALYL CHLORIDES

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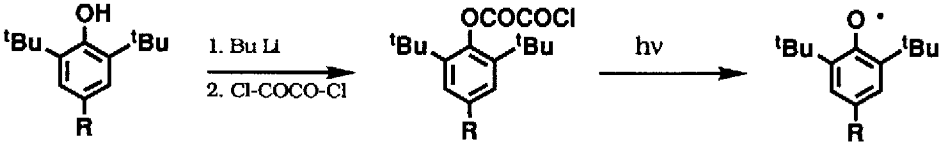
Abstract: UV photolysis of readily synthesized aryloxyoxalyl chloride half-esters provides a new unimolecular source of aryloxyl radicals, as shown by ESR and UV-vis spectroscopy.

Although phenoxyl radicals have been generated and investigated for a long time, such studies have usually been carried out under solution phase bimolecular oxidative conditions, or by direct photolysis of phenols.[1] We have recently had the occasion to desire a method for efficient unimolecular photochemical generation of phenoxyl and related aryloxyl radicals, and have found that aryloxyoxalyl chloride half-esters provide a readily available photochemical source of aryloxyl radicals.

Platz and coworkers have recently shown[2] that halogen substituted molecules can be convenient photochemical sources of some diradicals. Although in this method, a photochemical electron donor is usually required to cause loss of atomic chlorine and desired generation of radical centers, we felt that, by analogy, aryloxyoxalyl chlorides (AOC's) might undergo photolysis, presumably with production of the desired aryloxyl radicals, atomic chlorine, and two molecules of carbon monoxide.

Phenols **1-4**[3] were deprotonated using butyl lithium/hexanes and allowed to react with excess recently distilled oxalyl chloride. Removal of excess oxalyl chloride *in vacuo* followed by low temperature recrystallization in pentane gave product AOC's **5-8**.[4] Although sensitive to atmospheric water, these molecules appear to be reasonably stable at room temperature, and may be stored at -20°C under nitrogen for up to a month.

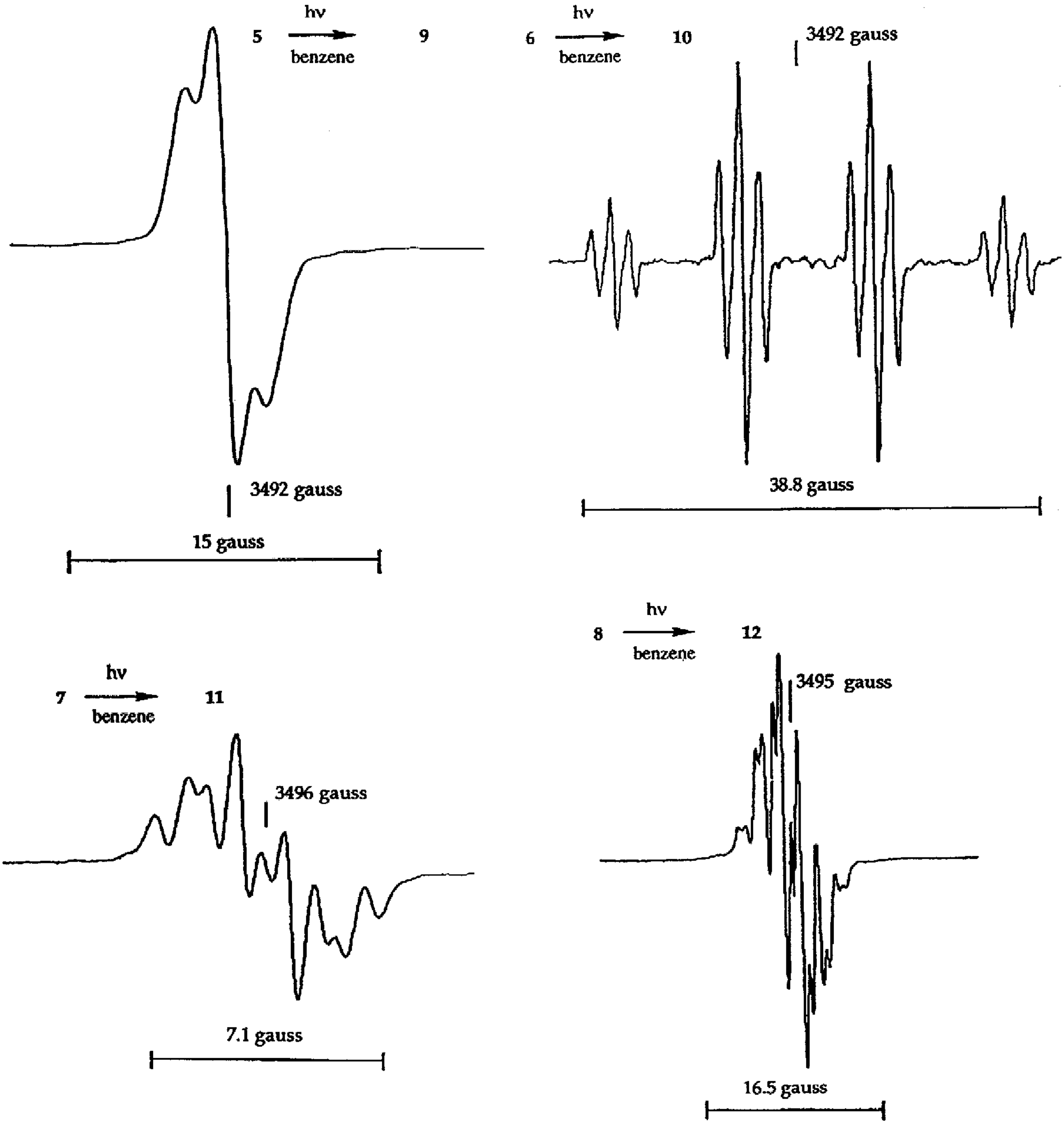


1 R = ^{t}Bu
2 CH_3
3 OCH_3
4 C_6H_5

5 R = ^{t}Bu
6 CH_3
7 OCH_3
8 C_6H_5

9 R = ^{t}Bu
10 CH_3
11 OCH_3
12 C_6H_5

Figure 1: ESR Spectra of Phenoxyl Radicals Generated by Photolysis of AOC's 5-8.



All spectra obtained in degassed benzene solution at room termperature at 9.79 GHz, after irradiation for 5-20 min with a 1000W Xenon arc lamp (Kratos). Midfields of each transition , and spectral width scales are indicated in each spectrum in gauss. Spectra were persistent for days under these conditions.

Upon photochemical irradiation of the samples (oxygen-free benzene, 1000 W Xenon arc lamp), strong, persistent ESR signals were observed, as well as color changes in the samples. Figure 1 (see preceeding page) shows typical ESR spectra obtained under these conditions, which are clearly due to the formation of sterically blockaded stabilized radicals **9-12**, as confirmed by comparison to ESR and UV-vis spectra generated by basic $K_3Fe(CN)_6$ oxidation of **1-4**.[5] The ESR spectra from our photochemical method were strong and remarkably free of obvious radical impurities, indicating the overall efficacy of the method.

Presumably photolysis causes initial cleavage of the C-Cl bond in the AOC's, followed by rapid loss of two molecules of carbon monoxide, a thermodynamically strong driving force that favors formation of the aryloxyl radicals. The final fate of atomic chlorine is not experimentally clear at this point, but it is notable that the ESR spectra of photolyzed AOC's are so free of impurities. In the photolysis of AOC **6**, for instance, atomic chlorine could potentially abstract a hydrogen atom from the *para*-methyl group, giving a benzyl radical that could be seen in the ESR. As the appropriate spectrum in Figure 1 shows, either this process does not occur, or such a resultant benzyl radical is too short-lived to be seen in our ESR experiments, since only the observed peaks are attributable to radical **10** (see however the accompanying paper).

Our photochemical method also works effectively under rigid matrix conditions, unlike previous solution oxidation methods. Photolysis of the AOC's at 77K in frozen benzene polycrystalline matrices gives ESR active samples that may be thawed to yield the very same ESR and UV-vis spectra[6] that are produced by simple solution phase photolysis, confirming the spectral assignments. Similar results are observed using frozen glassy matrices (methylcyclohexane, decahydronaphthalene, 2-methyltetrahydrofuran).

Besides tests of overall efficiency, a number of outgrowths and variations of this method may be easily envisioned. In addition to the well-known phenoxyl radical systems generated to test this method, a variety of previously unexamined phenoxyl radical species is under investigation in our group, using the synthetic techniques in this and the following paper under rigid matrix conditions and making characterization of these species possible without steric blockading of the oxyl radical center. In addition, other radicals may perhaps be generated by related chemistry, such as arylsulfyl and arylaminyl radicals. We are further exploring the potential uses[7] of this chemistry, and will report on such work in future publications.

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Research Corporation Grant. Some of these results were presented at the 197th American Chemical Society Meeting in Dallas, Texas on April 12, 1989.

REFERENCES

1. A. R. Forrester, J. M. Hay, R. M. Thomson, Chapter 7 of *Organic Chemistry of Stable Free Radicals;* Academic Press, New York, NY, 1968.

2. K. Haider, M. S. Platz, A. Despres, V. Lejeune, E. Migirdicyan, T. Bally, E. Haselbach, *J. Am. Chem. Soc.*, **110**, 2319(1988).

3. Phenols **1-3** were obtained from Aldrich Chemical Company and used without further purification. Phenol **4** was synthesized by the method of A. Rieker, P. Ziemek, *Z. Naturforsch.*, **206**, 640(1965) and gave satisfactory mp and spectral comparison to the literature references.

4. The AOC's were characterized by the following data. Their instability prevented distillation (of the oils) or consistent elemental analyses. Recrystallization of the solid AOC's was carried out in pentane at reduced temperature. In all cases, completeness of reaction was established by absence of the -OH band in the IR.

5 -- mp 52-54 °C. IR(CCl_4/cm^{-1}, C=O str): 1780, 1805(w, sh.)

^{1}HNMR($CDCl_3$, 80MHz): δ1.33(s,18), 1.34(s,9), 7.25(s,2)

6 -- (yellow oil). IR($CHCl_3$/cm^{-1}, C=O str): 1740, 1790(w. sh.)

^{1}HNMR($CDCl_3$, 80MHz): δ1.25(s,18), 2.26(s,3), 6.94(s,2)

7 -- mp 69-71 °C. IR($CHCl_3$/cm^{-1}, C=O str): 1750, 1780.

^{1}HNMR($CDCl_3$, 80MHz): δ1.26(s,18), 3.34(s,3), 6.89(s,2)

8 -- (yellow oil) IR($CHCl_3$/cm^{-1}, C=O str): 1760,1785.

^{1}HNMR($CDCl_3$, 80MHz): δ1.30(s,18), 7.2-7.7(m,7)

5. (a) E. Muller, R. Mayer, B. Narr, A. Schick, K. Scheffler *Just. Liebigs. Ann. der Chem.*, **645**, 1. (b) E. Muller, R. Mayer, B. Narr, A. Rieker, K. Scheffler *Just. Liebigs. Ann. der Chem.*, **645**, 25. (c) E. Muller, A. Rieker, R. Mayer, K. Scheffler *Just. Liebigs. Ann. der Chem.*, **645**, 53. (d) E. Muller, H. B. Stegman, K. Scheffler *Just. Liebigs. Ann. der Chem.*, **645**, 79(1961).

6. The UV region at < 300 nm for such hindered phenols has been described in C. D. Cook, D. A. Kuhn, P. Fianu, *J. Am. Chem. Soc.*, **78**, 2002(1956). For radical **10** rearrangement can occur (C. D. Cook, N. G. Nash, H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783(1955)), which presumably accounts for our difficulty in obtaining reproducible extinction coefficients in solution for this species. Qualitatively, **10** has absorptions at 392, 413, and 444 nm under conditions where the solution ESR spectrum described in the paper is observable. For the other radicals, the following absorptions (nm[ε]) are observed at > 300 nm: **9** -- 381[663]. 400[833], 620[162], **11** -- 389[2330], 403[1560], 433[1150], 534[108], **12** -- 485[2320], 532[sh,1130], 620[sh,554]. These spectra appear to be modestly stable under without special precautions, and are consistent with the general description of these radical spectra as described in G. Porter, E. J. Land, *Preprints of the International Symposium on Free Radicals, 5th, Uppsala*, **B4**, 1(1961).

7. During the preparation of this manuscript, we became aware of the recent use (independent of our work) of acid halides as photochemical sources of carbon-centered radicals. We thank Prof. Edwin Hilinski of Florida State University for advising us of this work in a private communication.

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