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CONVENIENT UNIMOLECULAR SOURCES OF ARYLOXYL RADICALS
II – ARYLOXYOXALYL *tert*-BUTYLPEROXIDES

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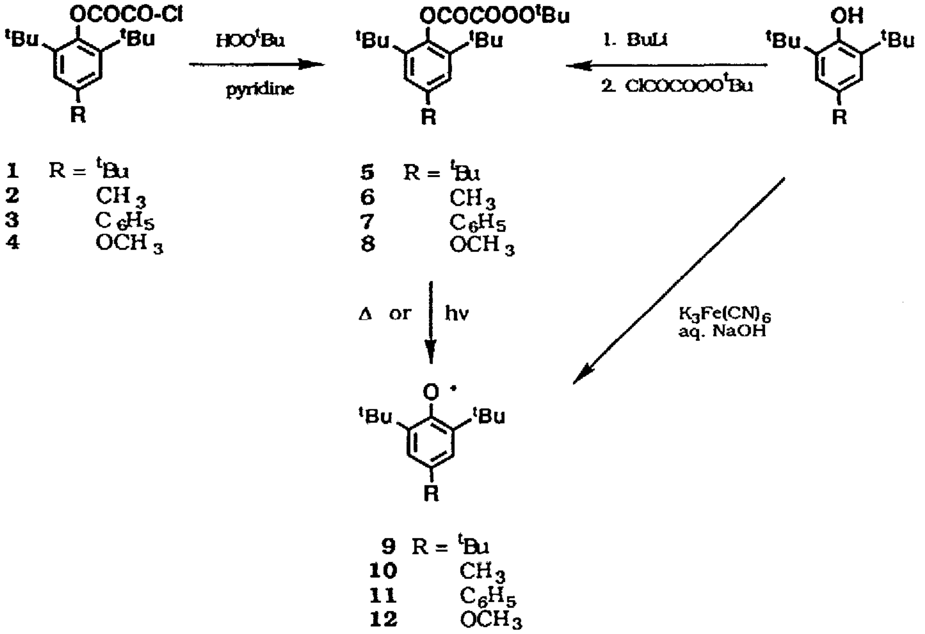
Abstract: UV photolysis and mild thermolysis of aryloxyoxalyl *tert*-butylperoxides provides a new unimolecular source of aryloxyl radicals, as shown by ESR and UV-vis spectroscopy.

As noted in the preceding paper,[1a] unimolecular methods for generating aryloxyl radicals[1b] -- especially under rigid matrix conditions -- appear generally to have been lacking, save for direct O-H photolysis in precursor phenols.[2] Hence efficient means to carry out aryloxy generation in matrix would be a useful addition to the variety of methods used for producing and studying radicals and polyradicals of related nature. In this communication we report the synthesis of some aryloxyl *tert*-butylperoxides and show their use as convenient, effective unimolecular photochemical and thermal aryloxyl precursors.

In one synthetic procedure, aryloxyoxalyl chlorides (AOC's) 1-4 were synthesized as in the preceding paper.[1] The appropriate AOC was then dissolved in dry diethyl ether and treated with one equivalent of *tert*-butyl-



hydroperoxide dissolved in ether/pyridine at 0°C, stirred for 30 min, then extracted sequentially using 10% $H_2SO_{4(aq)}$, 10% $NaHCO_{3(aq)}$, and water. The organic residue was dried over MgSO4 and evaporated to give the desired aryloxyl *tert*-butylperoxide (AOB), which may be recrystallized in pentane at low temperatures. AOB's **5-7**[3] were readily synthesized by this method, and appear to be quite stable at -20°C under nitrogen.

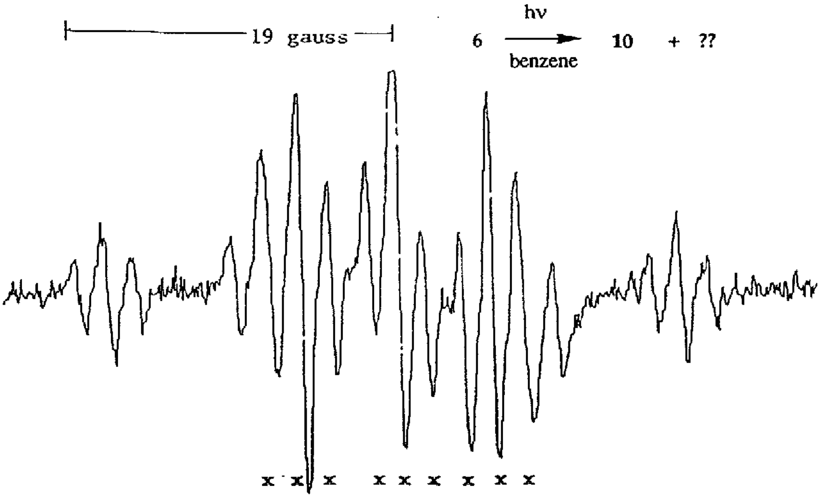
Attempts to make AOB **8** by this method failed. By an alternative procedure, efforts to add tert-butylperoxyoxalyl chloride (DANGER: EXPLOSION HAZARD4) to the lithium salt of 2,6-di-*tert*-butyl-4-methoxyphenol in benzene or pentane at below room temperature gave instant production of a deep red solution with UV-vis identical to that of the stable radical generated by oxidation of the phenol. ESR spectroscopy confirms that radical **12** is produced under these conditions, presumably through intermediacy of a highly unstable AOB **8**.

Irradiation of the stabler AOB's **5-7** (degassed benzene, unfiltered 1000 W Xenon arc) in solution quickly yielded the characteristic colors and UV-vis spectra of radicals **9-11**, with ESR spectra similar to those noted by solution oxidation of the corresponding phenols[5] and by photolysis of AOC's **1-3**.[1] The spectrum from photolysis of **6** also shows a radical impurity (x's, Figure 1, following page). The other spectra show no obvious similar impurities. We tentatively identify the unknown portion of the ESR in Figure 1 as being derived from chemistry following the hydrogen abstraction or rearrangement[6] in the active methyl group in **6** . Thermolysis of AOB's **5-7** (degassed benzene, 75°C, 15-60 min) yields bubbles, and is accompanied by the typical color changed indicating stable radical formation, with production of persistent ESR spectra confirming presence of **9-11**.

The lifetimes of radicals **9-11** appear substantially longer than those of the corresponding AOB's at elevated temperatures. Whereas solutions of **9-11** require overnight heating in benzene under nitrogen to discharge their color, observation of thermolysis of the AOB ester of phenol in CCl_4 at about 60°C shows complete depletion of the starting *tert*-butyl peak at δ1.38 ppm, and concurrent appearance of the decomposition product peak[7] at δ1.18 ppm (Figure 2, following page). The half-life of decomposition is approximately 90 min under these conditions. A more precise study of kinetics as a function of substituent R in the AOB's is in progress.

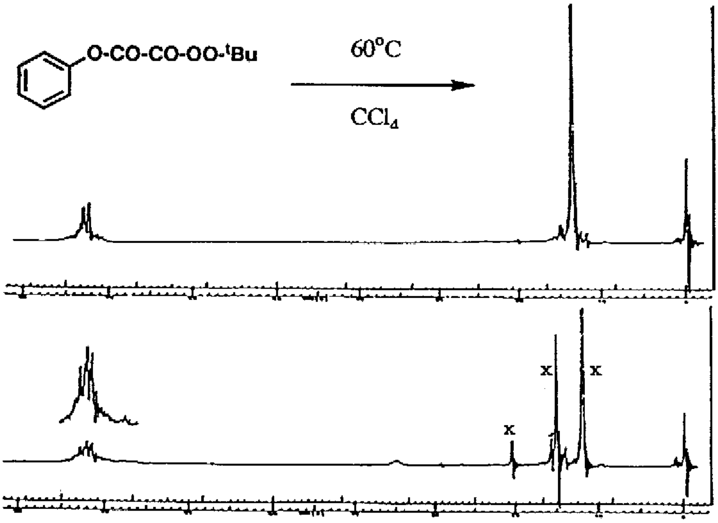
The utility of the AOB's is somewhat different from that of the AOC's described in the preceding paper. The stability of AOC's[1] seems somewhat greater than that of the AOB's, as shown by our failure to isolate AOB **8**. However, where the AOB's are stable they seem to be of near-equal photochemical utility as aryloxy precursors. In addition, AOB's readily produce aryloxyl radicals under very mild thermolytic conditions. We are particularly interested in the possibility that AOB's and related molecules may serve as aryloxy precursors at elevated temperatures in inert polymer matrices. These results and those of the preceding paper present two convenient, efficient unimolecular means for photochemical and thermal production of aryloxyl radicals in solution and in some rigid matrix

Figure 1: ESR spectrum Obtained from Photolysis of AOB ester 6.



The ESR spectrum was obtained in degassed benzene solution at room temperature at 9.79 GHz, after irradiation for 5-20 min with a 1000W Xenon arc lamp (Kratos). The spectral width scale is indicated in the spectrum in gauss. The suspected benzylic impurity peaks are indicated by x's -- other peaks are attributable to phenoxyl radical 10 by comparison to other spectra of 10.

Figure 2: ^{1}HNMR Spectra Following Thermal Decomposition of the AOB Ester of Phenol at 60°C.



Both ^{1}HNMR spectra were obtained at 60°C in carbon tetrachloride at 60 MHz. The upper trace shows the zero-time spectrum before significant reaction occurs, the lower trace shows the spectrum at a time of 19 h. X's in the lower trace indicate the final peaks of the decomposition products. The rightmost peak in the spectra is tetramethylsilane.

conditions. Other variations on the general theme of this work may readily be imagined. Further investigation of these possibilities and upon the decomposition mechanisms is in progress, and will be reported in due course.

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1. (a) D. A. Modarelli, F. C. Rossitto, P. M. Lahti *Tet. Lett.*, preceding paper in this issue. (b) Alkoxy radical generations methods are better known, *e.g.*, in the study of di-*tert*-butylperoxyoxalate by P. D. Bartlett, E. P. Benzing, R. E. Pincock *J. Am. Chem. Soc.*, **82**, 1769(1960).

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

4. These new compounds were characterized by spectral methods. Their instability prevented acceptably reproducible elemental analyses or safe distillation of **6**. The *tert*-butyl region of the proton NMR spectrum (δ 1.1-1.4 ppm) was particularly useful for evaluating purity of the samples.

5 -- mp 104-105 ^{o}C. IR($CHCl_3$/cm^{-1}, C=O str): 1760, 1780.

^{1}HNMR($CDCl_3$, 80MHz): δ1.35(s,18), 1.42(s,9), 1.46(s,9), 7.34(s,2)

6 -- (yellow oil). IR($CHCl_3$/cm^{-1}, C=O str): 1760, 1795

^{1}HNMR($CDCl_3$, 80MHz): δ1.21(s,18), 1.41(s,9), 2.28(s,3), 6.96(s,2)

7 -- mp 103-104 ^{o}C. IR($CHCl_3$/cm^{-1}, C=O str): 1760, 1790.

^{1}HNMR($CDCl_3$, 80MHz): δ1.40(s,18), 1.42(s,9), 7.2-7.7(m,7)

4. This compound was synthesized by reaction of excess oxalyl chloride with tert-butylhydroperoxide at reduced temperature. We recommend that it be made in amounts smaller than 2 g and stored under nitrogen at -20oC for short times only, and that it is best used as soon as synthesized. On one occasion a 5 g sample decomposed with considerable vigor upon being allowed to stand for an extended time at room temperature.

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. A dimerization reaction involving methyl hydrogen abstraction or rearrangement of radical has been described in C. D. Cook, N. G. Nash, H. R. Flanagan, *J. Am. Chem. Soc.*, *77*, 1783(1955). Products derivable from such a process may well give rise to the impurity spectrum. At present, we are still investigating as to what species may be causing this spectrum.

7. Although decompositions in various solvents give different product *tert*-butyl peaks, all give peaks at substantially different chemical shifts from the starting AOB esters. We have not yet made a full effort to characterize the *tert*-butyloxy derived products from this reaction, but intend to report further on these products when complete kinetic and product analysis studies have been completed.

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