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Synthesis of a new photochemical unimolecular precursor to aryloxy radicals is described, the bis-aryloxalate esters (BAO's). These molecules are readily synthesized, are thermally very stable, may be stored under ordinary benchtop laboratory conditions in the dark, make large and well-formed crystals, and are readily photolyzed either in solution or in solid phases. Solid state photochemical experiments may easily be carried out in polymer matrices (PPMA), frozen glassy matrix, microcrystalline powders, or in single crystals. Photoefficiency is about half by comparison to analogous aryloxyoxalyl *tert*-butylperoxide precursors (described in ONR Technical Report 12), but in symmetrical BAO's generated the same number of radicals per unit quantum of photolysis at 300 nm. Unsymmetrical BAO's are also readily synthesized from the oxalyl chloride half-esters of 2,4,6-tri-*tert*-butylphenol. Studies of radical-radical interaction in single BAO crystals are underway. BAO's may represent a good radical-generating moiety to attach to a polymer backbone in the generation of one-dimensional polyradicals.

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***Bis-ARYLOXALATES AS CONVENIENT UNIMOLECULAR
SOURCES OF ARYLOXYL RADICALS***

by David A. Modarelli and Paul M. Lahti*

Submitted for Publication in

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Bis-Aryloxalates as Convenient Unimolecular Sources of Aryloxyl Radicals

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Bis-aryloxalates (BAO's) 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 both previous and recent work involving phenoxy systems, generation of the desired radicals has typically involved solution phase chemistry. The classic studies by Mueller and coworkers³ of sterically blocked, stabilized phenoxy systems involved solution phase bimolecular oxidation with various reagents such as lead(IV) oxide, basic aqueous potassium ferricyanide, 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 described⁶ the synthesis and use of aryloxyoxalyl *tert*-butylperoxides and chlorides (AOB's **1** and AOC's **2**, respectively) as convenient *unimolecular* sources⁷ of aryloxyl radicals under solution conditions and in polymeric matrices. In this paper, we wish to report the use of *bis-aryloxalates* (BAO's, **3**) as unimolecular photochemical sources of phenoxyl radicals, and their superior stability and ease of use compared to our previously reported unimolecular aryloxy sources.

[INSERT SCHEME]

Symmetric 2,6-di-*tert*-butylated BAO's (**3**, $R_1 = R_1' = \textit{tert}$ -butyl) are readily synthesized by stirring oxalyl chloride with 2 equivs of the lithium salt of the corresponding phenol in diethyl ether at 0°C. BAO's are thermally much more stable than AOB's, 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 the AOB's all decompose at temperatures below 80°C. In the extreme case of 4-OMe substitution (1, $R_1 = \text{tert-butyl}$, $R_2 = \text{OMe}$), the AOB may not even be isolated, while the BAO (3, $R_1 = R_1' = \text{tert-butyl}$, $R_2=R_2'=\text{OMe}$) is readily prepared. As a result of AOB instability, repeated synthesis of small amounts of radical AOB precursor is typically needed, and the precursor must be stored at $<-20^\circ\text{C}$ in the dark. The AOC's are more thermally stable than the AOB's, but often tend to be extremely sensitive to atmospheric moisture (and possibly oxygen), degrading readily to the corresponding acids. In addition -- or possibly because of these reasons -- we have been unable to synthesize a number of AOC's that lack 2,6-di-*tert*-butyl substitution, but instead recover starting material or unidentified decomposition products. Yield of radicals from AOC's tend to be variable and low by UV-vis absorption and ESR spin count evaluation. Overall, we find that AOC's are not practically useful phenoxy precursors unless the positions *ortho* to the radical site are *tert*-butylated, and even these have short shelf-lives (less than one month). By contrast to both AOB's and AOC's, the BAO's 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 1000W Xenon arc, symmetric BAO's of 2,6-di-*tert*-butyl-4-substituted phenols give rise to the previously described⁸ persistent ESR and UV-vis spectra typical of the corresponding 2,6-di-*tert*-butyl-4-substituted phenoxyl radicals. No appreciable difference was noted between the stable radical spectra obtained by BAO photolysis and by PbO_2 oxidation of benzene solutions of appropriately substituted phenols. We find by comparative spin-counting ESR experiments that photocleavage of a BAO (3, $R_2=R_2'=\text{tBu}$) is only about half as efficient as that of the corresponding AOB, but with two possible radicals per monomer leads to approximately the same yield of radicals per unit time per quantum. Overall, we find that BAO's are effective solution photochemical radical sources. In addition, BAO's photolyze well in rigid media, such as degassed frozen 2-methyltetrahydrofuran or degassed polymethylmethacrylate (PPMA) cast films. The PPMA films are particularly convenient as rigid matrices for

ESR and UV-vis spectral samples, and are optically clear up to 10% BAO by weight. Finally, most of the BAO's 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 spectral studies of intermolecular spin-spin interaction of geminate radical pairs in the solid state.

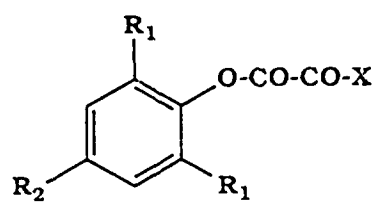
Finally, we have found that synthesis of unsymmetrical BAO's ($R_n \neq R_n'$) is straightforward, if the relatively stable 2,4,6-tri-*tert*-butylphenolic AOC (**2**, $R_1 = R_2 = R_3 = \text{tert-butyl}$, **246 TBP-AOC**) is coupled with various phenols as described earlier. We find the relative stability of **246-TBP-AOC** to make this method practically useful for unsymmetrical BAO's. Also, the ESR spectrum of the corresponding 2,4,6-tri-*tert*-butylphenoxy (**246TBP-O**) is distinct and relatively narrow (~ 12G wide in solution, about 3-4 times broader in solid matrix). As a result, with some account taken of the narrow resonance from the **246TBP-O** leaving group radical, we can generate and detect by ESR radicals with intrinsically broader spectra, such as *p*-stilbeneoxy⁹ generated at 77K in a neat BAO powdered solid sample or in 5% PPMA film. This raises the possibility of using BAO's as convenient groups for photochemical generation of multiple pendant phenoxy sites on a molecule or polymer chain.

Our findings, taken with our earlier results for AOB's and AOC's, 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 phenoxy generation under rigid conditions have not been commonly employed, save for some phenol photolyses.¹⁰ Given recent interest in synthesizing high-spin organic poly-radicals,¹⁻² we hope that AOB's and BAO's 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.

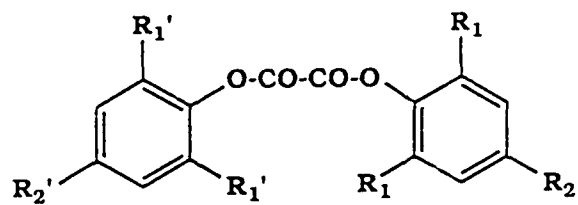
This work was supported by the Office of Naval Research, and the Exxon Education Foundation. ESR spectra were obtained at the Department of Polymer Science and Engineering at the University of Massachusetts at Amherst, on an IBM Instruments ESP-300 ESR spectrometer that was purchased with the aid of a grant from the International Business Machines Corporation.

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5. S. A. Weiner, *J. Am. Chem. Soc.*, **94**, 581(1972). S. A. Weiner and L. R. Mahoney, *Ibid.*, **94**, 5029(1972).
6. D. A. Modarelli, F. C. Rossitto, and P. M. Lahti *Tet. Lett.*, 4473, 4477(1989).
7. A unimolecular thermal method of generating stable phenoxyl radicals from symmetrical bis-cyclohexadien-4-one peroxides is described in C. D. Cook and M. Fraser, *J. Org. Chem.*, **29**, 3716(1964).
8. Cf. refs. 6 for ESR and UV-vis descriptions of phenoxyl radicals prepared from AOB's and AOC's, which were the same as spectra obtained in the present work.
9. We have previously observed this radical from photolysis of the corresponding AOB. Cf. D. A. Modarelli, F. C. Rossitto, M. Minato, and P. M. Lahti, *Proc. Mater. Res. Society Sympos.*, **173**, 0000(1990), in the proceedings from the meeting cited in reference 2.
- 10 Cf. A. R. Forrester, J. M. Hay, and R. M. Thomson in *Organic Chemistry of Stable Free Radicals*; Academic Press, New York, NY, 1968; Chapter 7.



- 1 $X = OO-tert-Bu$
 2 $X = Cl$



3

Supplementary Material for

Bis-Aryloxalates as Convenient Unimolecular Sources of Aryloxyl Radicals

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Synthesis of Diphenyl Oxalate: This general reaction is a useful preparative method for any unhindered diaryl oxalate. Phenol was used as received. Oxalyl chloride was distilled under vacuum. Pyridine was distilled from barium oxide. The oxalyl chloride (2.62 g, 20.6 mmol) was dissolved in 30 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0°C for 15 min. Phenol (4.86 g, 51.6 mmol) and pyridine (3.48 g, 41.3 mmol) in ether were added via an equilibrating addition funnel, precipitating a white solid. After stirring for 1 h, the ether solution was washed with 10% H₂SO₄, sat'd Na₂CO₃, and water. The solid was filtered, redissolved in methylene chloride, and dried over MgSO₄. Evaporation under reduced pressure afforded 3.57g of a white powder (71%, mp. 131-132°C*) which was recrystallized from 95% ethanol.
 IR(Nujol mull, cm⁻¹): 1753, 1731 (C=O); 1189, 1161 (C-O).
 NMR(CDCl₃, 80MHz): δ 7.18-7.6(m)

* Known compound. See Adickes, Brunnert, Luecker, *J. prakt. Chem.*, **130**, 163(1931).

Synthesis of Bis(2,4,6-Tri-*t*-butylphenoxalate): Tri-*t*-butyl phenol was distilled under vacuum and recrystallized from hexane at -78°C. Oxalyl chloride was distilled under vacuum. The phenol (7.25 g, 27.64 mmol) was dissolved in 40 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0°C for 15 min. *n*-Butyl lithium (17.83 mL, 27.64 mmol, 1.3M) was then syringed in, precipitating a white solid which was stirred for 10 min, before oxalyl chloride (1.754 g, 13.82 mmol) in ether was added via an equilibrating addition funnel, precipitating a pinkish-white solid. After stirring for 1 h, the ether solution was washed with 10% H₂SO₄, sat'd Na₂CO₃, and water. Drying over MgSO₄ and evaporating the ether under reduced pressure afforded 7.30 g of a whitish powder which was recrystallized from 95% ethanol to yield (4.88 g, 61%, mp 240-241°C).

IR(Nujol mull, cm⁻¹): 1755cm⁻¹ (C=O); 1189, 1161 (C-O).
 NMR(CDCl₃, 80MHz): δ 1.36(18H, s), 1.48(36H, s), 7.39(4H, s).
 Elemental -- Theor C 78.84, H 10.10, Found C 79.12 H 9.93.

Bis(4-Methoxy-2,6-di-*t*-butylphenyl)oxalate: Oxalyl chloride was distilled under vacuum. 4-Methoxy-2,6-di-*t*-butyl phenol was used as received. The phenol (1.00 g, 4.23 mmol) was dissolved in 15 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0°C for 15 min. Butyl lithium (3.25 mL, 4.23 mmol, 1.3 M in hexanes) was then syringed in, precipitating a white solid which was stirred for 10 min, before oxalyl chloride (0.269 g, 2.11 mmol) in ether was added via an equilibrating addition funnel, precipitating a pinkish-white solid. After stirring for 1 hr, the ether solution was washed with 10% H₂SO₄, sat'd NaHCO₃, and water. Drying over MgSO₄ and evaporating the ether under reduced pressure afforded 0.91 g of a whitish powder (78%, mp. 79-81°C). (An attempted recrystallization from boiling 95% ethanol yielded only the phenol, indicating that at higher temperatures, the *p*-methoxy BAO is thermally unstable.)

IR(Nujol mull, cm⁻¹) 1749, 1790 (C=O); 1180, 1165 (C-O).
NMR(CDCl₃, 80MHz) δ1.41(36H, s), 3.78(6H, s), 6.78(4H, s)

Synthesis of Phenoxy-,2,4,6-Tri-*t*-butylphenoxy Oxalate: Tri-*t*-butyl phenol was distilled under vacuum and recrystallized from hexane at -78°C. Oxalyl chloride was distilled under vacuum. Phenol was used as received. Pyridine was distilled from barium oxide. The tri-*t*-butyl phenoxalyl chloride (AOC) was prepared in the usual manner.⁶ The AOC (1.720 g, 4.87 mmol) was dissolved in 15 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0°C for 15 min, before a solution of the phenol (0.382 g, 4.06 mmol), and pyridine (0.341 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 then washed with 10% H₂SO₄, sat'd Na₂CO₃, and water. Drying over MgSO₄ and evaporating the ether under reduced pressure afforded a brownish-white solid which was recrystallized from 95% ethanol to yield white rod-like crystals (0.8223 g, 49%, mp. 104-105°C).

IR(Nujol mull, cm⁻¹): 1752, 1771 (C=O); 1176, 1153 (C-O).
NMR (CDCl₃, 80MHz) δ1.34(9H, s), 1.41(18H, s), 7.20-7.50(5H, m).
Elemental -- Theor. C 76.06 H 8.35, Found C 76.29 H 8.49.

Synthesis of *p*-Stilbeneoxy-2,4,6-Tri-*t*-butylphenoxy Oxalate: Tri-*t*-butyl phenol was distilled under vacuum and recrystallized from hexane at -78°C . Oxalyl chloride was distilled under vacuum. 4-Hydroxystilbene was used as received (Aldrich Chemical). Pyridine was distilled from barium oxide. The tri-*t*-butyl phenoxalyl chloride (AOC) was prepared in the usual manner.⁶ The AOC (1.55 g, 4.38 mmol) was dissolved in 15 mL of anhydrous ether and stirred under a nitrogen atmosphere at 0°C for 15 min, before a solution of the stilbene (0.575 g, 2.92 mmol), and pyridine (0.246 g, 2.92 mmol) in 35 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 10% H_2SO_4 , sat'd Na_2CO_3 , and water. Drying over MgSO_4 and evaporating the ether under reduced pressure afforded 1.39 g of an off-white solid (93%, mp. $164\text{--}165^{\circ}\text{C}$) which was recrystallized from 95% ethanol.

IR (Nujol mull, cm^{-1}): 1769, 1748 (C=O); 1181, 1168, 1150, 1130 (C-O); 968 (*trans* HC=CH).

NMR (CDCl_3 , 80MHz) δ 1.34(9H, s), 1.41(18H, s), 7.00-7.70(13H, m).
Elemental -- Theor. C 79.65 H 7.86 Found C 79.40 H 8.04.

General Procedure for the Preparation of a BAO Polymethylmethacrylate Film -- The polymethylmethacrylate (PMMA) and the BAO, usually ~10% by weight, are dissolved in 15 mL methylene chloride, swirled for a few minutes to ensure adequate mixing, nitrogen is bubbled through for 10 more minutes, and the solution is poured into an aluminum evaporating dish. The aluminum dish is placed inside a dessicator and dry nitrogen blown through for until tacky. The dessicator is then placed under vacuum (sometimes aspirator pressure to prevent bubbling of the film, and then full vacuum). Placing the dessicator under vacuum for ~30 min is then usually sufficient to get rid of excess methylene chloride, to be fully dried, however, ~2-3 h is necessary. The film is carefully peeled out of the evaporating dish, ready for use. These films are transparent to the eye, and appear to be stable indefinitely.

Spin-count experimental procedure: The phenoxy precursors were cast into poly-methylmethacrylate (PPMA, Aldrich) matrices by dissolution of both precursor and PPMA in nitrogen degassed chloroform and removal of the solvent under vacuum. The films were stored at -20°C in the dark under nitrogen. Diphenylpicrylhydrazide (DPPH, Aldrich, 95%) was also cast into PPMA films in a similar fashion. UV-vis analysis of the DPPH films established that no appreciable decay of the DPPH occurred on the time scale of the spin count experiments.

Small pieces of the PPMA films (~1.5mmX4mm) were cut, placed in an ESR tube, evacuated, and then irradiated at 77K for 30min (the exact same distance was kept for each photolysis by using two dewars - one for photolysis and one for ESR measurements. Transfer was made from photolysis dewar to a transport dewar to the ESR dewar as quickly as possible to prevent condensation on the ESR tubes prior to insertion into the ESR dewar. Modulation amplitude, number of computer averaged scans, and the receiver gain were held constant during the experiments.

Some sample calculations are shown below:

Calculation of the spectrometer frequency ν :

$$\begin{aligned}\nu &= g\beta H/h \\ &= (2.0036)(9.27410 \times 10^{-21} \text{ erg G}^{-1})(3426.200 \text{ G}) \\ &\quad \text{-----} \\ &\quad 6.6262 \times 10^{-27} \text{ erg s} \\ &= 9.6080 \times 10^9 \text{ Hz}\end{aligned}$$

Calculation of the g-value:

$$\begin{aligned}g &= h\nu/\beta H \\ &= (6.6262 \times 10^{-27} \text{ erg s})(9.6080 \times 10^9 \text{ Hz}) \\ &\quad \text{-----} \\ &\quad (9.72410 \times 10^{-21} \text{ erg G}^{-1})(3423.710 \text{ G}) \\ &= 2.0050\end{aligned}$$

To calculate the number of spins present in the DPPH standard:

$$\begin{aligned}\text{NDPPH} &= [(\text{Molarity of film})(\text{weight of portion of film} \\ &\quad \text{used})/(\text{density of film})][\text{portion of spins per molecule}] \\ &= [(2.97 \times 10^{-6} \text{ mol/mL})(.0046 \text{ g})/(1.188 \text{ g/mL})][0.95]^\lambda \\ &= 1.0925 \times 10^{-8} \text{ moles of radical} = \text{number of spins}\end{aligned}$$

^λThe number 0.95 is the correction due to the amount of DPPH present in the material from Aldrich. See also Alger, R.S. "Electron Paramagnetic Resonance: Techniques and Applications" John Wiley and Sons, New York, 1968, p204.

The computational method to determine spin count for all radical samples relative to the integrated spin intensity of the DPPH standard sample are described in J. E. Wertz, J. R. Bolton, Electron Spin Resonance -- Elementary Theory and Practical Applications, Chapman and Hall, New York, NY, 1986; Appendix D, p. 462ff.

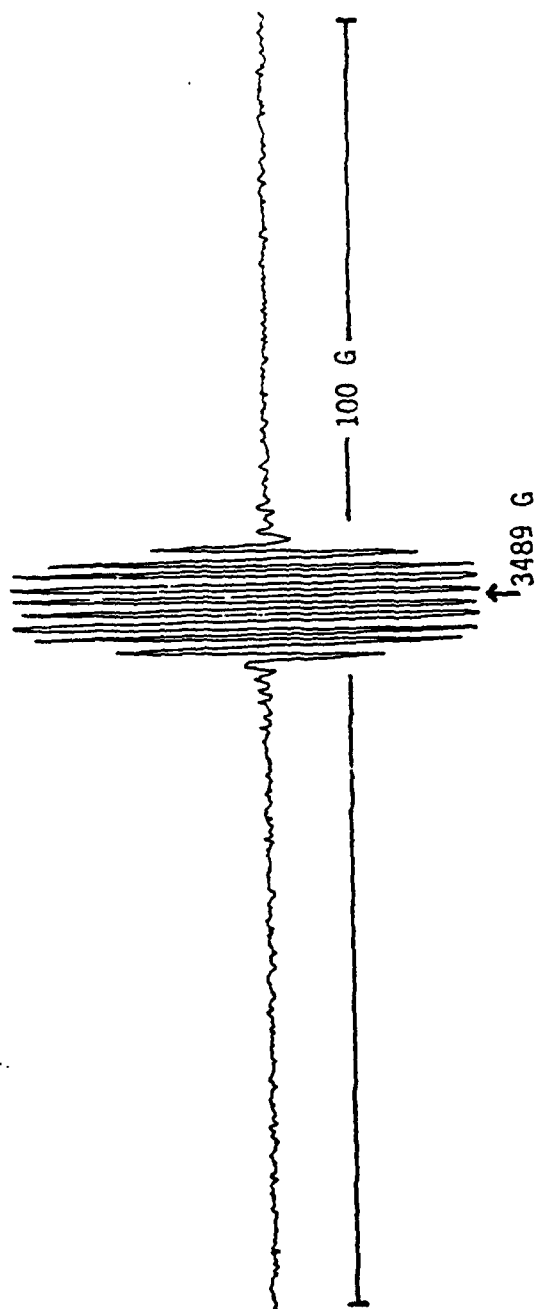
Based upon the number of radicals produced and the number of moles present in the the photolyzed sample relative to the moles of precursor in the weighed portion of polymer film, the spin conversion in the time interval could be computed. We did not attempt in these experiments to irradiate to constant radical concentration, which is reached in about 3 hours with our photolysis equipment.

Caption to Electron Spin Resonance Spectra.

All ESR spectra were recorded at 9.608 GHz on an X-band spectrometer. Structures of photolyzed precursors are identified by reference to the text of the manuscript. For each spectrum, the scale of the transitions is indicated in Gauss. All spectra were centered in the typical region for organic radicals, about 3490 G on our spectrometer.

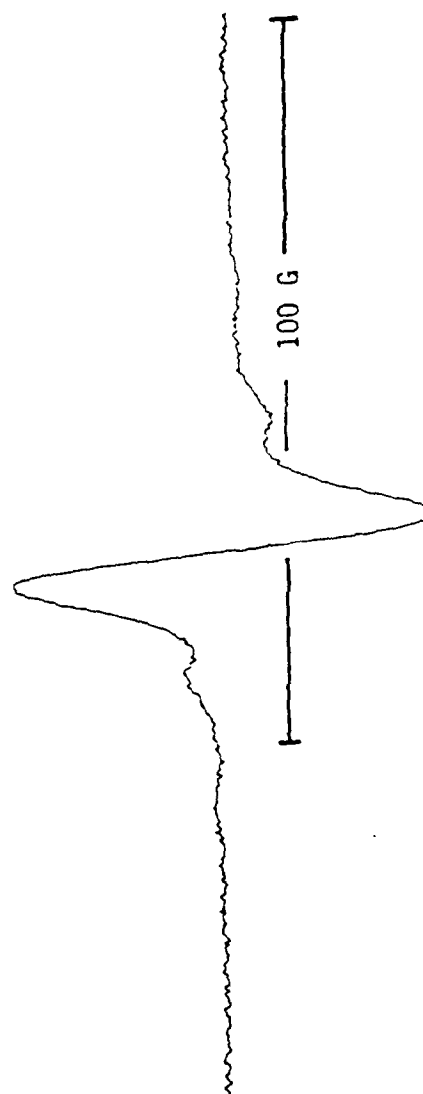
For the p-stilbeneoxy spectrum, transitions associated with the stilbeneoxy were identified by comparison spectra obtained by us in reference 9 of the manuscript, and are marked with an "S". A small, unidentified peak is marked with an "X".

Compound 3 ($R_1 = C(CH_3)_3$; $R_2 = OCH_3$) photoalyzed
in PhH at 27°C

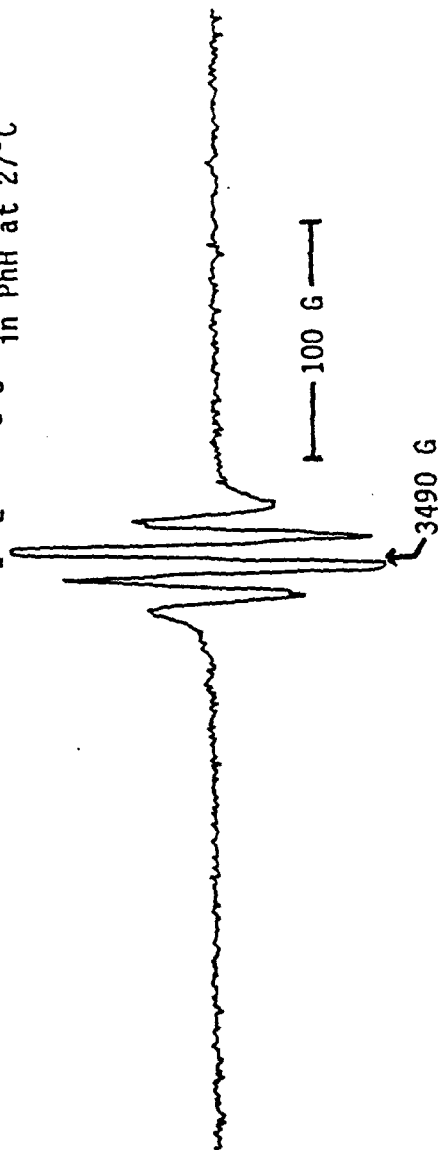


viii

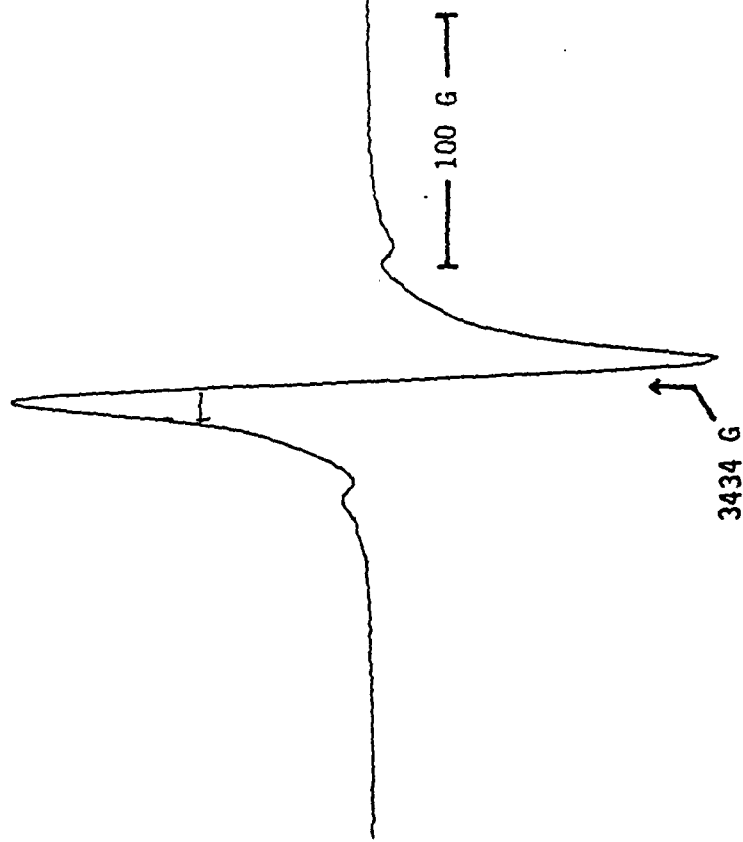
Compound 3 ($R_1 = C(CH_3)_3$; $R_2 = OCH_3$) neat powder
photoalyzed at 77 K



Compound 3 ($R_1=R_2=C(CH_3)_3$) photolyzed
in PhH at 27°C

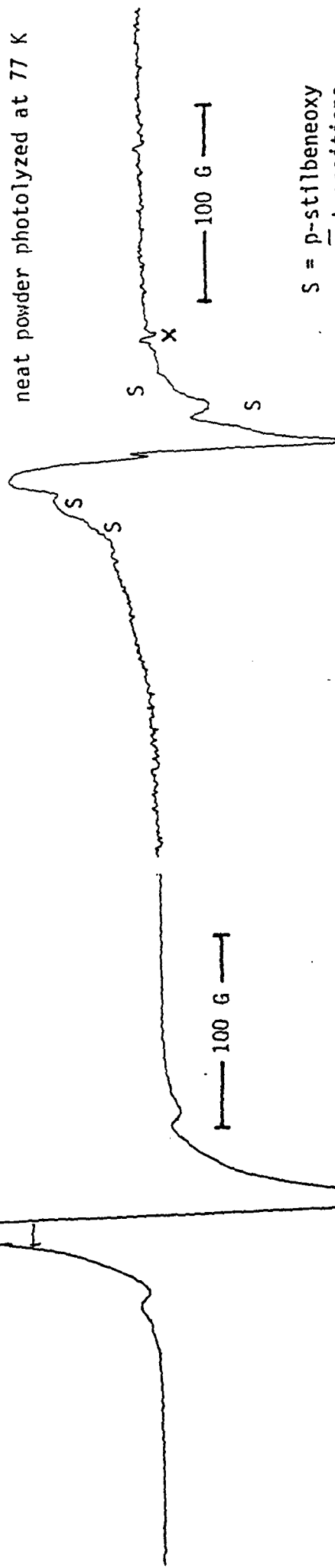


Compound 3 ($R_1=R_2=C(CH_3)_3$) neat powder
photolyzed at 77 K



ix.

Compound 3 ($R_1=C(CH_3)_3$; $R_2=C(CH_3)_3$; $R_1'=H$; $R_2'=\text{trans Cl=CH-Ph}$)
neat powder photolyzed at 77 K



S = p-stilbeneoxy
transitions