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Synthesis and Photolysis of N-(Phenoxycarbonyloxy)-2-thiopyridone Derivatives. A New Unimolecular Route to Quantitative Generation of Phenoxyl Radicals

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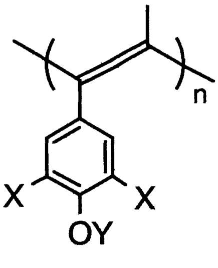
N-(Phenoxycarbonyloxy)-2-thiopyridone derivatives were prepared by the reaction of lithium phenoxides with phosgene followed by the reaction with 2-mercaptopyridine N-oxide and photolyzed to give quantitative yield of phenoxyl radicals.

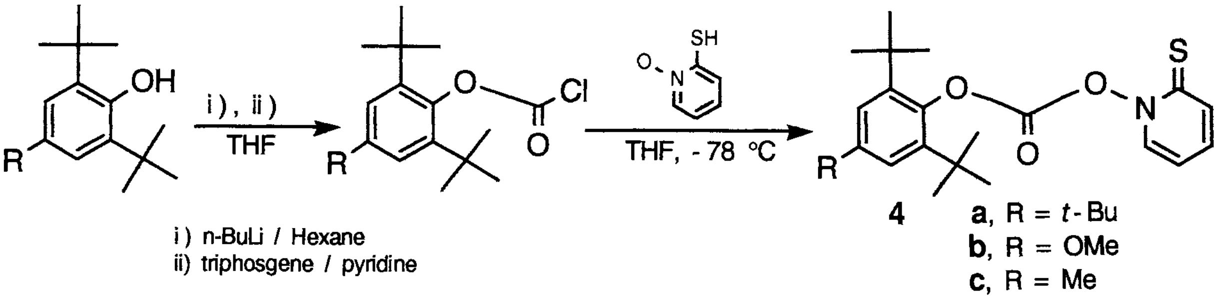
Organic ferromagnets are one of the most interesting subjects of current chemistry.$^{1)}$ Ovchinnikov proposed in 1978 on the basis of a valence bond theory that a polyacetylene **1** carrying phenoxyl radicals as pendants might become an organic ferromagnet.$^{2)}$ Inspired by this proposal, Nishide et al. tried to synthesize poly(ethynyl-phenoxyl) **2**. Whereas a reasonable sample of the precursor polyphenol **3** was obtained, the yield of the phenoxyl radicals as estimated by ESR signal intensity was very low (less than ca. 10%).$^{3)}$ This is most probably due to solution-phase bimolecular oxidation used for the generation of the phenoxyl radicals. Under these conditions, they are free to recombination and/or disproportionation.$^{4)}$ Unimolecular generation of phenoxyl radicals in solid or solid solution where diffusion of free radicals is restricted is highly desirable.



1, X = H Y = •
2, X = *t*-Bu Y = •
3, X = *t*-Bu Y = H

Some phenol drivatives are known to generate the phenoxyl radicals by photolysis, but the reaction is far from efficiency.$^{5)}$ Phenyl acetates undergo photo-Fries rearrangement. However, not much phenoxyl radicals escape from the radical pair in the solvent cage.$^{6)}$ Lahti et al. reported the synthesis and use of phenoxyoxalyl t-butyl peroxides and chlorides as convenient unimolecular photochemical sources for phenoxyl radicals.[7)] But these precursors are not so stable and their ESR spectra always show many additional signals due to impurities concomitantly formed by irradiation. For our purpose, these impurities will interfere with magnetic measurements. It is highly desired to develop a new efficient precursor for generating phenoxyl radicals cleanly. For this purpose, we prepared the N-(phenoxycarbonyloxy)-2-thio-pyridone derivatives **4**, and studied their photolytic behaviors as phenoxyl radical precursors.

The esters **4** were synthesized by the reaction of phosgene (from triphosgene and pyridine in a 1: 3 molar ratio) with the lithium salt of the corresponding phenols for 2 h followed by the reaction with 2-mercaptopyridine N-oxide in THF at -78 °C (Scheme 1).



Scheme 1.

The products **4a** and **4b** were recrystallized from n-pentane to give colorless microcrystals in 60 and 26% yields, respectively, and identified by their NMR and IR spectra (Table 1).[8,9)] The esters **4** are stable at room temperature and decomposed slightly only at about 120 °C.

Table 1. ^{1}H-NMR and IR Spectral Data of N-(Phenoxycarbonyloxy)-2-thiopyridones **4**[a)]

	2-t-Bu 6-t-Bu	4-R	3-H 5-H	Thiopyridone residue	$\nu_{C=O}$ /cm^{-1}
4a	1.40 (s)[b)]	1.32 (s)	7.36 (s)	7.20-7.32 (m)	1744
(R=tert-Bu)	1.40 (s)		7.36 (s)	8.28-8.32 (m)	
4b	1.38 (s)	3.81 (s)	6.88 (s)	7.18-7.34 (m)	1748
(R=CH_3O)	1.38 (s)		6.88 (s)	8.25-8.32 (m)	
4c	1.38 (s)	2.33 (s)	7.13 (s)	7.20-7.30 (m)	1743
(R=CH_3)	1.38 (s)		7.13 (s)	8.25-8.29 (m)	

a) Recorded on a 270 MHz NMR spectrometer in $CDCl_3$ at an ambient temperature. b) Numbers for NMR data are chemical shift values in ppm from internal TMS. s and m denote singlet and multiplet, respectively.

The photochemical reactions of **4** were carried out under various conditions and monitored by ESR, UV/VIS and IR spectra. Thus, irradiation of **4a** in freshly distilled and degassed benzene at room temperature with a mercury lamp (the light of the wavelength longer than 320 nm was used) gave **5a** in 30 seconds, as judged by the rapid appearance of ESR signals and UV/VIS absorptions that were characteristic of the phenoxyl radical obtained by well-known chemical method: oxidation of the phenol with PbO_2.[4] Any impurity was not found at all (Fig. 1). Absorbance at λ_{max} = 625 nm gave an estimate of almost quantitative yield of **5a** (Fig. 2). Irradiation in a frozen toluene matrix at 50 K gave the similar spectra.

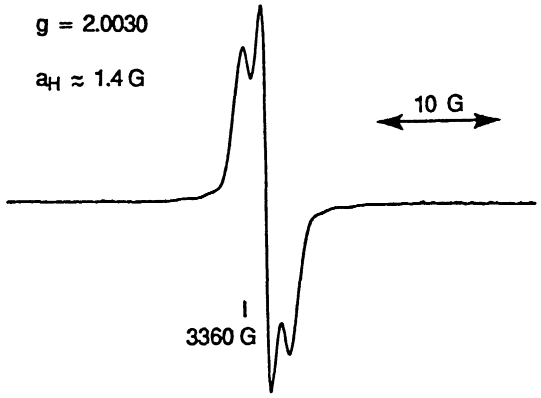


Fig. 1. X-Band ESR spectrum (low resolution) of **5a** in benzene at room temperature.

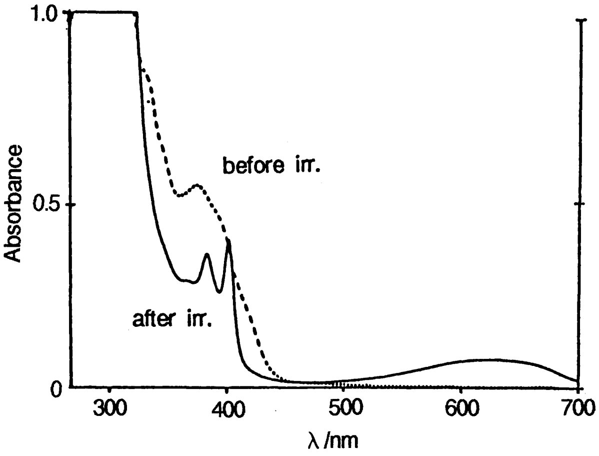
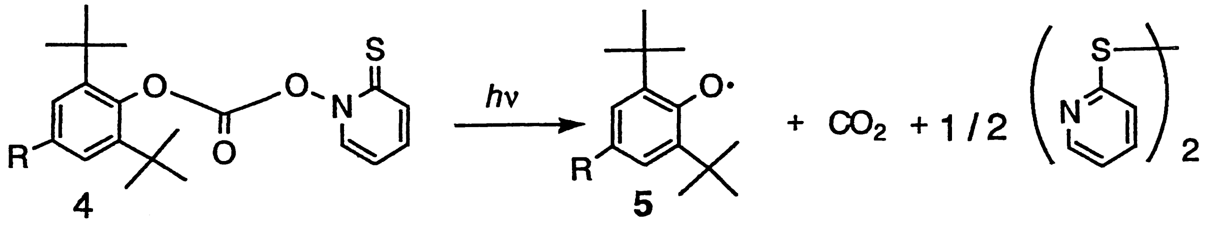


Fig. 2. UV/VIS spectra of **4a** (before irr.) and **5a** (after irr.) in benzene.

When the KBr pellet of **4a** was irradiated similarly, peaks due to the phenoxyl at 1670 and 1610 cm^{-1} and a peak due to carbon dioxide at 2300 cm^{-1} appeared quickly at the expense of an absorption at 1744 cm^{-1} assigned to the carbonyl group of **4a**.

The other esters **4b** and **4c** were photolysed in a similar fashion to give the corresponding phonoxyl radicals. These observations show that **4** decompose entirely into phenoxyl radicals, carbon dioxide, and thio radical under photolysis. The thio radical may be rapidly dimerized,



Scheme 2.

because no other signals except phenoxyl radicals appeared in ESR spectra (Scheme 2). Overall, we found that esters **4** are extremely effective unimolecular sources of phenoxyl radicals in both fluid and solid solutions. These precursors and photolytic reaction can serve as the phenol counterpart of one of the Barton reactions$^{10)}$ in which alkoxyl radicals are generated efficiently, and have the following merits: (1) esters **4** are very stable even at room temperature, (2) readily converted into phenoxyl radicals in an excellent yield, and (3) without forming other impurities.

We consider that these compounds can be applied to the synthesis of organic polyradicals, and the preparation of a stoichiometric sample of magnetically interesting poly(ethynyl-phenoxyls) is in progress.

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8) ^{13}C NMR spectral data of **4a** are as follows: ($CDCl_3$) δ 31.5, 31.8, 34.9, 35.6, 123.5, 123.6, 125.8, 126.9, 138.8, 141.5, 145.3, 145.8, 148.3.
9) **4** gave satisfactory elemental analyses.
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