The Sulfuranyl Radical Structure and Reactions of *o*-(Thio)benzoyloxyl Radicals Formed by the Decomposition of *t*-Butyl *o*-(Thio)-perbenzoates Studied by ^{1}H and ^{13}C CIDNP and ^{17}O NMR

Warō Nakanishi,* Yoshiaki Kusuyama, Yoshitsugu Ikeda, and Hiizu Iwamura*,†
Department of Chemistry, Faculty of Education, Wakayama University, Masagocho, Wakayama 640
†*Division of Applied Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444*
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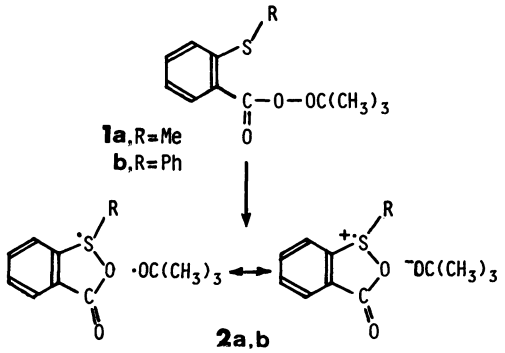
^{1}H and ^{13}C CIDNP signals were observed in the methyl group of *o*-(methylthio)benzoic acid and the methylene group of 3,1-benzoxathian-4-one (**6**) during the thermal decomposition of *t*-butyl *o*-(methylthio)perbenzoate. The results show that the free "*o*-(methylthio)benzoyloxyl radical" itself is better represented as the bridged sulfuranyl radical in which most of the spin density is localized at the sulfur atom rather than in the carboxyl. Thermolysis of *t*-butyl *o*-(methylthio)- and *o*-(phenylthio)perbenzoates-*carbonyl*-^{17}O was carried out and the oxygen labels were detected by ^{17}O NMR spectroscopy preferentially at the carbonyl oxygen of **6** and diphenyl 2,2′-dithiodibenzoate ruling out the zwitterionic radical structure. The migration of phenyl group and the peroxomonosulfate oxidation of *o*-(phenylthio)benzoic acid are also discussed.

The rate of thermolysis of *t*-butyl perbenzoate is enhanced by the substitution at the *ortho* positions with iodo,[1] vinyl,[2] and thio[1,3] groups. In the case of *t*-butyl *o*-(methylthio)- and *o*-(phenylthio)perbenzoates (**1a** and **1b**, respectively), for example, the rate acceleration reaches upwards of 10^4 times relative to the unsubstituted system (**1e**) at 60 °C in chlorobenzene. The decomposition proceeds with the significant lower $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values.[1] The transition state is also considered to accompany a considerable polar character[4] as shown in the susceptibility of the rate of the thermal decomposition of **1b** to the substituents, solvent ionizing powers, and added salts. Martin *et al.*



2a,b

proposed a mechanism of the homolytic O–O bond cleavage anchimerically assisted by the neighboring sulfur atom with structure **2** contributing to the transition state.[1] The heavy atom effect as seen in *o*-iodo derivative[5] was excluded here and the steric acceleration was not important because *o*-(*t*-butyl) derivative showed little rate enhancement.[1]

The question we want to raise is if the sulfuranyl radical structure (**3** and/or **4**) should only be the contributing structure in the transition state for the thermolysis reaction or could also be an important representation of the resulting "*o*-(thio)benzoyloxyl radicals." Our strategy was two-fold: The CIDNP method and ^{17}O labeling technique. The CIDNP method has been employed to the elucidation of a number of free radical reaction mechanisms.[6] When applied to the structural study of 2-chloroethyl,[7] 2-bromoethyl,[8] phenethyl,[7] and neophyl[9] radicals, only the classical structures were concluded. In the present case, the cyclic sulfuranyl radical *vs.* "*o*-(thio)benzoyloxyl radical" will be answered by the CIDNP effect in the S-methyl protons and carbon.[10] Secondly, in contrast to the ^{18}O tracer technique[11] widely used to elucidating structures and reaction mechanisms in organic chemistry, the ^{17}O labeling coupled with ^{17}O NMR determination[12] has not been very much publicized and yet has the strong advantage as a nondestructive method; by employing chemical shifts and integration of the signal intensities, the site and distribution of the isotopes in the product molecules can be determined directly.

^{17}O NMR spectroscopy has now been applied to thermal decomposition of ^{17}O labeled *t*-butyl *o*-(methylthio)- and *o*-(phenylthio)perbenzoates (**1a*** and **1b***, respectively).[12]

Quite independently from ours, Martin *et al.* treated the problem by using ESR spectroscopy.[13]

Results and Discussion

The CIDNP Results. Thermolysis of *t*-butyl *o*-(methylthio)perbenzoate (**1a**) produces *o*-(methylthio)-benzoic acid (**5a**: 30%), 3,1-benzoxathian-4-one (**6**: 12%), *t*-butyl alcohol (62%), and acetone (21%) in chlorobenzene at 70 °C.[1]

When a solution of 5 mg of **1a** in 0.5 ml of *o*-dichlorobenzene was heated at 80 °C in a ^{1}H NMR probe, strong emission (E) and enhanced absorption (A) signals were observed at δ 2.38 and 5.21, respectively (Fig. 1).[14] By adding a small amount of the authentic samples to the completed reaction mixture and observing increase in the corresponding signal intensities, it was found that the methyl protons of **5a** were in E and methylene protons[15] of **6** were in A. The signals due to acetone and *t*-butyl alcohol were not spin-polarized. CIDNP was not clear in the aromatic protons for the reaction run in tetrachloroethylene or decalin. The ^{13}C experiments of **1a** were carried out on a solution of 150 mg of **1a** in 1 ml of *o*-dichlorobenzene at 75 °C.

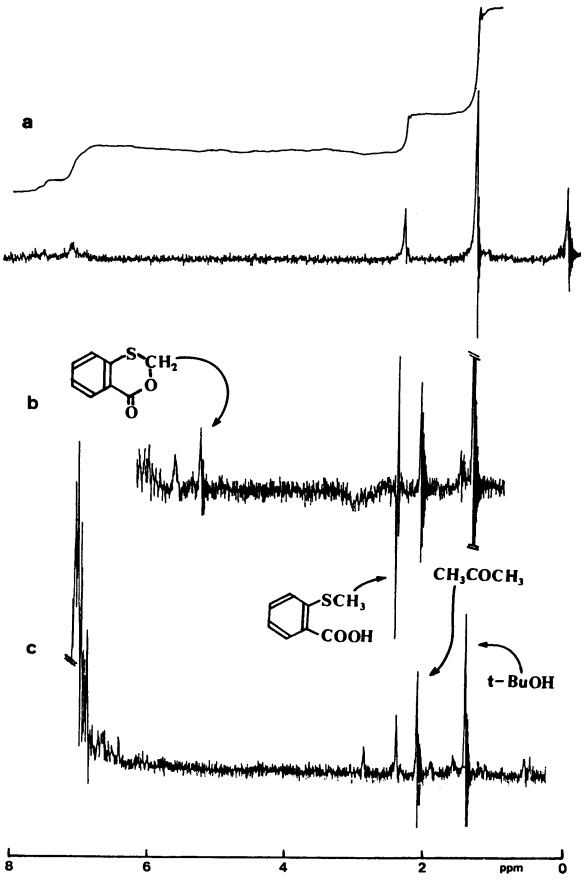


Fig. 1. ^{1}H NMR spectra of **1a**. a: In carbon tetrachloride at 27 °C, b: during the decomposition in *o*-dichlorobenzene at 80 °C, c: after the reaction at 80 °C.

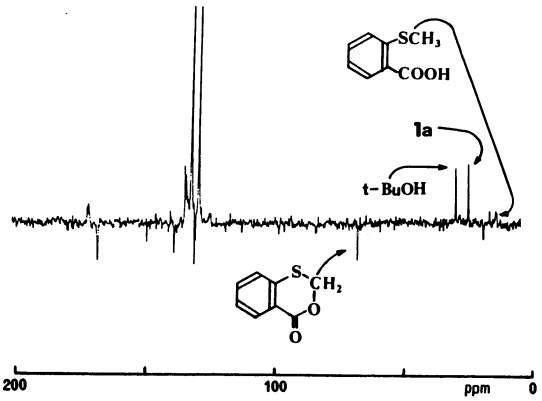
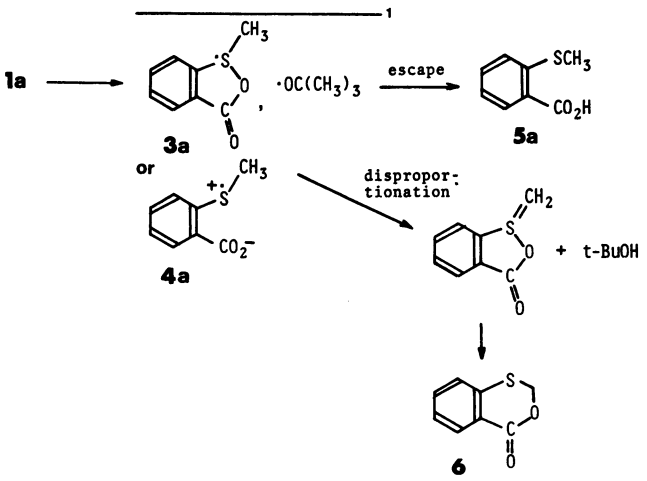


Fig. 2. ^{13}C CIDNP spectrum obtained during the decomposition of **1a** in *o*-dichlorobenzene at 75 °C. See also Ref. 16.

As shown in Fig. 2, the methylene carbon of **6** was in strong E at δ 68.7. The *S*-methyl carbon of **5a** at 15.5 was in A. There were some polarization signals yet to be assigned in the aromatic carbons. There were no polarization signals in the C=O carbon region of **5a** and **6**.[16]

All the results, especially strong polarization in the *S*-methyl group and no polarization in the carbonyl carbons in **5a** and **6** indicate that hyperfine interactions of the methyl protons and carbons are quite large and that the considerable spin density must be localized at the sulfur atom and not in the carboxyl group in the "*o*-(methylthio)benzoyloxyl radical" (**3a**). This is in accordance with the ESR measurement of **3a** and a close analog of **3a** performed by Martin *et al.*[13] The *g*-value of **3a** is 2.0080 and the proton hyperfine splitting of *S*-methyl group is 9.0 G and that of aromatic proton *ortho* to carbonyl group is 1.5 G. The ESR results are best interpreted in terms of a bridged radical with an S–O bond, in which the odd electron is in a σ-type orbital with a large spin density on sulfur. The sign for hyperfine coupling are expected to be plus for the β-H and minus for the α-C in the methyl group of *S*-centered radical **3a**.

The CIDNP spectra are reasonably explained only when the radical has structure of **3a** (or **4a**). In reference to the Kaptein rule,[6b] Scheme 1 is proposed for the observed CIDNP.

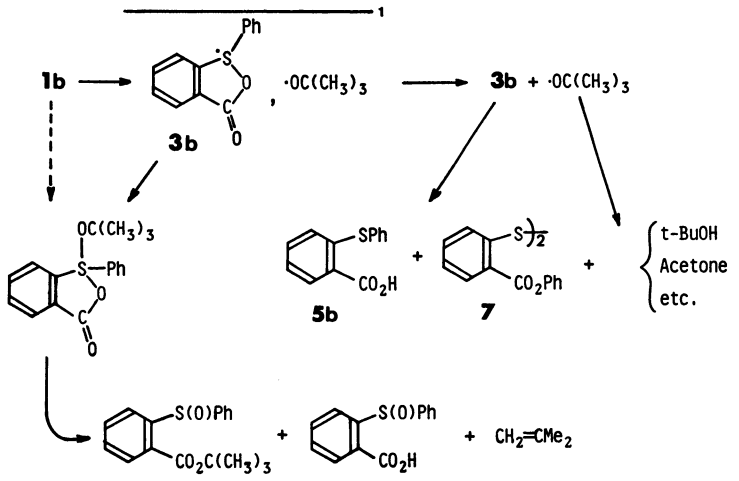


Scheme 1.

$$\Gamma_{ne}(i) = \mu\varepsilon\Delta g A_i,$$

where the sign of polarization of nucleous i due to the net effect ($\Gamma_{ne}(i)$) is given by the product of signs of the spin multiplicity of the precursor, the mode of the reaction, the difference in the *g* factors in the radical pair, and the hyperfine coupling constant of nucleus i. The Δg term is negative for **3a** because *g*-value of **3a** is 2.0080 while that of *t*-butoxyl radical is 2.009.[14] The opposite signs of polarization found in the *S*-methyl group of **5a** and the methylene group of **6** are reasonably ascribed to the different mode of formation of these products:[6] **5a** is an escape product ($\varepsilon<0$) while ε for **6** is positive which may be formed by cage-disproportionation followed by rearrangement.

Similar CIDNP experiments on *t*-butyl *p*-(methylthio)perbenzoate and the *o*-methoxyl derivative (**1c**) gave negative results. The ^{1}H signals due to acetone, *t*-butyl alcohol, and methyl protons of *p*-(methylthio)-benzoic acid of the products increased monotonically during the decomposition of *t*-butyl *p*-(methylthio)-perbenzoate in hexachlorobutadiene at 155 °C. No CIDNP was observed in the methoxyl groups of anisole and *o*-methoxybenzoic acid in thermolysis of **1c** in *o*-dichlorobenzene at 147 °C.



Scheme 2.

CIDNP experiments were also carried out on the thermolysis of *t*-butyl *o*-(phenylthio)perbenzoate (**1b**). Some polarized signals were observed in the phenyl carbon region, but none of them could be assigned to *o*-(phenylthio)benzoic acid (**5b**), diphenyl 2,2′-dithiodibenzoate (**7**), or *o*-(phenylsulfinyl)benzoic acid. Strong polarization was ascribed only to the solvent reacted products. The decomposition mechanism of **1b** proposed by Martin *et al.* is shown in Scheme 2.[3c]

Thus the CIDNP experiments clearly exhibit that most of the spin density should be localized at the sulfur atom. This is possible only when the radical has either the cyclic sulfuranyl radical (**3a**) or a zwitterion radical (**4a**) structure. The "*o*-(thio)benzoyloxyl radical" structure is very unlikely.

Decomposition of ^{17}O-labeled Peroxy Esters. As an operational test to differentiate between the two possibilities, we had recourse to the ^{17}O labeling technique in which the carbonyl oxygen of the starting peroxy esters was specifically enriched with ^{17}O and distribution of the isotope in the cyclic product was examined. Unfortunately scrambling of the two oxygen sites in the carboxyl group did not allow us to study the ^{17}O distribution in the major product **5a**.

Thermal decomposition of *t*-butyl *o*-(methylthio)-perbenzoate enriched with ^{17}O selectively at the carbonyl group (**1a***) was carried out in chlorobenzene at 76 °C. Carbonyl oxygen in **1a*** is estimated to be enriched by *ca.* 4.6 atom%. The contribution from the natural abundance isotope to ^{17}O NMR spectra is less than 1%, since natural abundance of ^{17}O is only 0.037 atom%.

^{17}O-labeled 3,1-benzoxathian-4-one (**6***) was isolated as a decomposition product. As shown in Fig. 3, the ^{17}O NMR spectrum of the lactone contains two signals: The downfield signal (365 ppm from external D_2O) due to the carbonyl oxygen and the higher one (159 ppm) due to the ether oxygen.[17] They were found to be in the integration ratio of 66 : 34. The ratio was 50 : 50 when the ^{17}O NMR spectrum of **6** in natural abundance was measured. Thus the oxathianone-*carbonyl*-^{17}O (**6***[**C**=**O***]) and the oxathianone-3-^{17}O (**6***[–**O***–]) were found in the ratio of 66 : 34 when **1a*** was decomposed under the conditions described above.[18] As shown in Table 1, the formation of **6***[**C**=**O***] in preference to **6***[–**O***–] was more favored as the temperature of decomposition was lowered.

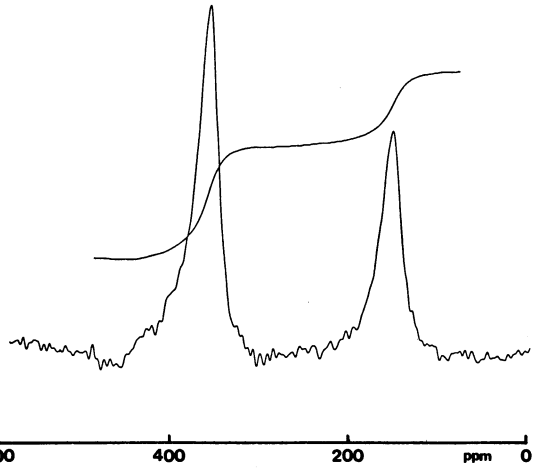
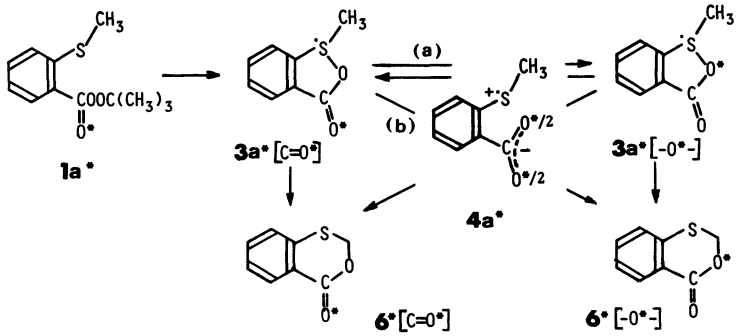


Fig. 3. ^{17}O NMR spectrum of **6*** derived from the thermal decomposition of **1a*** at 76 °C.

Table 1. Population of the ^{17}O label in **6** and the temperature of decomposition of **1a***

Temperature/°C	**6***[**C**=**O***]	**6***[–**O***–]
76	66	34
62	69	31
40	74	26

A similar study has been carried out on the decomposition of *t*-butyl *o*-(phenylthio)perbenzoate-*carbonyl*-^{17}O (**1b***). Thermolysis of **1b** gives diphenyl 2,2′-dithiodibenzoate (**7**) among many other products as shown in Scheme 2.[1,3c] ^{17}O-labeled **7** (**7***) was isolated as a decomposition product of **1b*** in chlorobenzene at 52 °C. Here we encountered a typical example showing the limitation of the ^{17}O NMR method. Since the line width of ^{17}O NMR signals is governed by quadrupolar relaxation, line broadening of the signal becomes serious as the size (represented by a^3 of a spherical molecule of the radius *a*) of molecules increases.

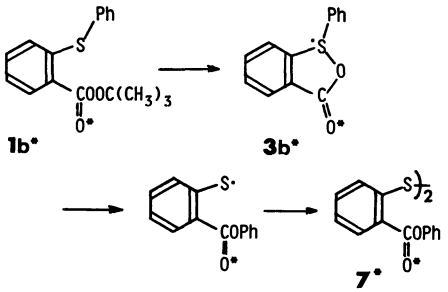


Scheme 3.

Whereas the signal due to the ^{17}O enriched carbonyl oxygen was easily determined, it was difficult to get a reasonable S/N for ^{17}O poor ether oxygen of **7***. Therefore a strategy of carrying out the measurement on a smaller molecule was adopted. Population of the ^{17}O label was thus determined on phenyl *o*-mercaptobenzoate obtained by cleavage of the S–S bond of **7*** into two halves by the method of Overman *et al.*[19] Integration of the peaks at δ 363 and 191 for the carbonyl and ether oxygens, respectively, gave a ratio of 71 : 29.

Martin and Koenig[2b] investigated the distribution of ^{18}O in 3-benzhydrylphthalide obtained from the decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate labeled with ^{18}O in the carbonyl position. By comparing the content of the ^{18}O isotope before and after the saponification/relactonization procedure, it was found that the identity of the carbonyl oxygen of the phthalide was in 88% retention.

As shown in Scheme 1, thermal decomposition of **1a** produces **5a** and **6** as escape and disproportionation products, respectively, of the primary radical pair formed by the O–O bond cleavage of **1a**.[1] If the anchimerically assisted O–O bond cleavage takes place by intramolecular electron transfer from the sulfur to the antibonding O–O orbital and the structure of "*o*-(methylthio)benzoyloxyl radical" formed is **3a**, **6***[**C**=**O***] should be exclusively formed from **1a***. Structure **4a** should operationally lead to scrambling of the label between the two oxygen atoms, although there may be some lifetime before the requisite rotation of the Ar–CO_2^- bond takes place. The results in Table 1 indicate that the identity of the carbonyl oxygen can be kept through the reaction path to lactone **6*** and that there is a competitive channel available for the scrambling of the oxygen label which has the higher activation energy of the reaction than that retentive path by 2.3 kcal/mol. The scrambling of the label between the carbonyl and endocyclic oxygens may take place either before or during the course of the Pummerer type rearrangement (a or b in Scheme 3). Zwitterionic radical is supposedly an intermediate or a transient species in these scrambling processes. Therefore it is concluded that the "*o*-(methylthio)benzoyloxyl radical" should be described as cyclic structure **3a**. However the contribution of the induced decomposition[1] which could be another mechanism for the retention of oxygen label may take place in the decomposition of **1a**.* In



Scheme 4.

the case of **1b***, the contribution of the induced decomposition such as **1a*** is negligible.[1] The 71% of ^{17}O retention in the carbonyl oxygen of **7*** well establishes the sulfuranyl radical structure **3b** for the "*o*-(phenylthio)benzoyloxyl radical" (Scheme 4).

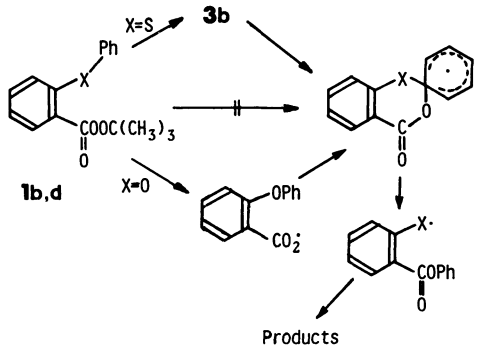
Thus the sulfuranyl radical structure has been well established by a combination of CIDNP and ^{17}O NMR spectroscopy.

Phenyl Migration in o-*Phenoxy- and* o-*(Phenylthio)-benzoyloxyl Radicals.* DeTar and Hlynsky[20] reported predominant phenyl migration in *o*-phenoxybenzoyloxyl radical produced by the decomposition of bis(2-phenoxybenzoyl) peroxide. In this study, the decomposition of *t*-butyl *o*-phenoxyperbenzoate (**1d**) was examined. As shown in Table 2, the decomposition rate constant for **1d** in chlorobenzene at 132 °C is 4.13×10^{-4} s^{-1} which is almost as fast as that calculated from the kinetic parameters (ΔH^*=33.5 kcal/mol and ΔS^*= 7.8 e.u.)[21] of *t*-butyl perbenzoate (**1e**) at the temperature. Phenyl salicylate was produced in 7—10% in this reaction.[22] The rate constant for the decomposition of *t*-butyl *o*-methoxyperbenzoate (**1c**) was also determined as 5.23×10^{-4} s^{-1} in chlorobenzene at 118 °C. The rate constant is 6.7 times larger than that estimated for nonsubstituted one. *o*-Methoxybenzoic acid was produced in *ca.* 40% yield at 118 °C. However it was

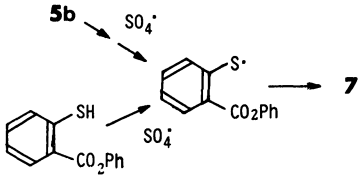
Table 2. Rate constant for decomposition of *t*-butyl *o*-(oxy)perbenzoates

Compound	k/s^{-1}	(Temp/°C)	k_{rel}
1c	5.23×10^{-4}	(118)	6.7
1d	4.13×10^{-4}	(132)	1.1
1e[a]			1.0

a) Ref. 21.



Scheme 5.



Scheme 6.

ca. 10% at 132 °C in chlorobenzene with the formation of anisole in *ca.* 10%.

As also suggested by Martin,[1] the oxygen atom *ortho* to the peroxy ester moiety does not play an important role in the O–O bond homolysis, that is, anchimeric assistance is absent in *o*-(oxy)perbenzoates. By comparing the rate constant for **1d** with those of **1c** and nonsubstituted one, participation of phenyl ring can be excluded (Scheme 5). Therefore, the phenyl migration in **1b** and **1d** is explained by a two step mechanism. The phenyl migration in **3b** occurs *via* 1,2-shift of the phenyl group in sulfuranyl radical.[1] In the case of **3d**, the ipso attack by the carboxyl radical to the phenoxyl group may occur. The direct attack of the phenyl group to O–O bond is negligible.

The rearranged thiyl radical was directly formed by potassium peroxomonosulfate oxidation[23] of phenyl *o*-mercaptobenzoate. Treatment of phenyl *o*-mercaptobenzoate with equimolar peroxomonosulfate in boiling water gave **7** in 90—95% yield. Oxidation of *o*-(phenylthio)benzoic acid (**5b**) with peroxomonosulfate resulted in the formation of 30% of **7** and *ca.* 10% of by-products with *ca.* 60% of recovery of the starting material. In the presence of catalytic amount of silver ion and 3 molar excess peroxomonosulfate, the yield of **7** was very much improved. The formation of **7** from H-abstraction of **5b** shows that the phenyl migration also occurs in this case (Scheme 6).

Experimental

^1H spectra were obtained on a JEOL C 60HL spectrometer operating at 60 MHz. ^{13}C spectra were obtained on a Varian PFT 80 CFT 20 Pulse Fourier Transform spectrometer operating at 20.1 MHz or on a JEOL FX-60Q spectrometer operating at 15 MHz.

CIDNP Measurement. For a typical run, a solution of 5 mg of **1a** in 0.5 ml of chlorobenzene was sealed in a 5 mm ϕ NMR sample tube. ^1H NMR spectra were measured at room temperature. Then the sample was put into an NMR probe preheated at 80 °C. The CW ^1H NMR spectra were obtained at 20 s, 60 s, and so on after the sample tube was brought into the probe. Time-dependent spectra containing polarized signals were obtained. After the reactions were over, a small amount of authentically prepared compounds was added to assign the CIDNP signals. The chemical shifts were determined from acetone, one of the products, as δ 2.18.

^{13}C CIDNP spectra were obtained in a similar manner on a solution of 150 mg of **1a** in 1 ml of *o*-dichlorobenzene at 75 °C using a Varian CFT-20 spectrometer. A 8 μs pulse was applied with an acquisition time of 0.909 s over the spectral width of 4.5 kHz. The number of data points was 8 K and the number of transients accumulated was *ca.* 300.

As solvents, chlorobenzene, *o*-dichlorobenzene, tetrachloroethylene, 1,1,2,2-tetrachloroethane, hexachlorobutadiene, and decalin were employed after distillation and checked by ^1H NMR.

^{17}O NMR Measurement. ^{17}O NMR spectra were measured on a Varian FT-80A spectrometer at 10.782 MHz, using a 90° pulse of 0.02 s. A spectral width was 8000 Hz with 323 data points, the Fourier number being kept at 16384. The labeled sample (*ca.* 300 mg) was dissolved in chloroform-*d* and the temperature of the probe was set at 60 °C in order to obtain a better S/N of the signals due to narrower half-band widths. A reasonable S/N of *ca.* 8 of the spectra was obtained by 1 h's accumulation (the number of transients accumulated was 10^5) for enriched samples of this size of molecules. Three to four such data were averaged; the reporoducibility of the relative peak areas was ±2%.

Materials. *t*-Butyl *o*-(methylthio)- and *o*-(phenylthio)-perbenzoates (**1a** and **1b**, respectively) and 3,1-benzoxathian-4-one (**6**) were prepared in analogy with Martin's method.[1] Physical properties agreed well with those in the literature.

t-Butyl o-Methoxyperbenzoate (1c) and t-Butyl o-Phenoxyperbenzoate (1d). These compounds were prepared in a similar manner to that for **1a** and **1b**.

1c: Recrystallization from pentane-ether after low temperature chromatography on basic alumina. Mp 52.0—52.5 °C. Found: C, 64.43; H, 7.31%. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%.

1d: Purified by chromatography on basic alumina with ether as an eluent at low temperature. Colorless oil. Found: C, 71.19; H, 6.28%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

^{17}O Enriched o-(Methylthio)benzoic Acid (5a).* Sodium hydroxide 2.2 g (55.6 mmol) and 1 g of water enriched with ^{17}O in 20 atom% (Prochem, 55.6 mmol) were dissolved in 80 ml of dioxane in the presence of a small amount of 18-crown-6. Then 10.36 g (55.6 mmol) of *o*-(methylthio)benzoyl chloride in 20 ml of dioxane was added at 70 °C, and refluxed for 10 h. After evaporation of the solvent, the mixture was acidified with cold diluted hydrochloric acid (*ca.* 0.005 mol dm^{-3}). The precipitate was washed with cold water and recrystallized from hot water yielded 7.77 g (83%). Mp 169—170 °C (lit,[24] 169 °C). From Mass spectra, the *o*-(methylthio)benzoic acid prepared above was enriched with ^{17}O by 9.1%. So each oxygen in **5a*** is enriched with ^{17}O by 4.6%.

t-Butyl o-(Methylthio)perbenzoate-carbonyl-^{17}O (1a).* To a solution of 5.0 g (31 mmol) of 1,1′-carbonyldiimidazole in 100 ml of THF was added a solution of 5.0 g (30 mmol) of **5a*** in 50 ml of THF, then stirred at 40 °C for 2 h.[25] After evolution of carbon dioxide, 5.4 g (60 mmol) of *t*-butyl hydroperoxide in THF (50 ml) was dropped at −10 °C, and stirred for 2 h. After one night at −20 °C, the solvent was evaporated *in vacuo* below 0 °C. Then cold ether was added and washed with cold water as soon as possible. After drying

over calcium chloride at low temperature, the solvent was evaporated below 0 °C. The residue was purified by chromatography on basic alumina with ether as an eluent at −15 °C. Five and three tenth grams (74%) of **1a*** was obtained. Physical properties and ^{1}H and ^{13}C NMR spectra of **1a*** were the same as those of **1a**.

t-Butyl o-(Phenylthio)perbenzoate-carbonyl-^{17}O (1b).* This compound was prepared in the same manner as that for **1a***.

*Decomposition of 1a**. A solution of 5.3 g of **1a*** in 69 ml of chlorobenzene was stirred at 76 °C for 30 min under nitrogen atmosphere. The solvent was removed *in vacuo*. The residue was chromatographed on silica gel with chloroform as an eluent. Pure **6*** (327 mg) was obtained with 300 mg of a mixture of **6*** and **5a***.

*S–S Bond Cleavage of 7**. Decomposition of **1b*** was carried out similarly at 52 °C and **7*** was isolated. Then **7*** (95 mg) and 52 mg of triphenylphosphine were dissolved in 2 ml of dioxane. The solution was acidified with 0.5 ml of 0.02 mol dm^{-3} hydrochloric acid and kept under nitrogen at 40 °C for 1 h. After removing most of the solvent under reduced pressure, the risidue was extracted with ether, dried over anhydrous magnesium sulfate and chromatographed on silica gel to give 73 mg of phenyl *o*-mercaptobenzoate[19] enriched with ^{17}O.

Oxidation of 5b with Potassium Peroxomonosulfate. To a suspention of 1.0 g of **5b** in boiling water (30 ml) was added a solution of 1.17 g of potassium peroxomonosulfate in 20 ml of water and refluxed for 3 h.[23] After cooling and acidified with diluted hydrochloric acid, crude products were obtained. The crude products contained **7** (30%), **5b** (*ca.* 60%), and by-products. When the mixture was chromatographed on basic alumina, **7** and one of by-products were isolated. In the presence of silver ion and 3 molar excess peroxomonosulfate, the yield of **7** was very much increased but that of the by-product was not improved and occasionally it was not found in the mixture.

Oxidation of phenyl *o*-mercaptobenzoate with peroxomonosulfate yielded 90—95% of **7** without silver ion.

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