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Dramatic Change of Carbonyl Oxide Reactivity by the Potent Electron-Withdrawing Trifluoromethyl Group

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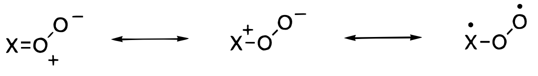
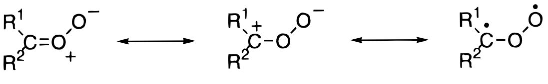
α,α,α-Trifluoroacetophenone oxide, generated by $^1O_2$ oxidation of $Ph(CF_3)CN_2$, reacted electrophilically with sulfoxides ($\rho = -0.74$ vs σ; $r = 0.95$) affording sulfides as the major product. The intermediacy of persulfoxides formed via cyclic peroxidic sulfuranes in the novel deoxygenation was evidenced by an ^{18}O-tracer study and by the formation of benzaldehyde in the reaction with benzyl phenyl sulfoxide. Olefins were oxidized to epoxides during the photooxidation of $Ph(CF_3)CN_2$. From the fact that the epoxidation proceeded almost stereospecifically and the substituent effect on styrenes resulted in the negative ρ-value of -1.66 vs σ ($r = 0.97$), a dioxirane was proposed as the second intermediate which might be formed by the isomerization of carbonyl oxide. Trapping experiments with styrenes and sulfoxides suggested that the cyclization of carbonyl oxide is competitive with the reaction with sulfoxides. In contrast to the known nucleophilic nature of carbonyl oxides, the present oxide is shown to have an electrophilic character, indicating that the reactivity of carbonyl oxides could be controlled by substituents.

Introduction

The structure and chemical properties of 1,3-dipolar peroxidic species **1** such as ozone (X = O), nitroso oxides (X = R−N), and carbonyl oxides (X = R_2C) have been attracting much attention from synthetic, biological, and theoretical standpoints.[1] These active oxygen species have similar electronic structures formulated as zwitterions (**1a**, **1b**) and/or biradical form (**1c**), and their reactivities may be altered depending on the nature of X.[2] Typically, ozone[3] and nitroso oxides[4] have an electrophilic character reflecting their biradical structure (**1c**). On the other hand, carbonyl oxides **2**,[5] which are important intermediates in the ozonolysis[3] of olefins and as a model for monooxygenase enzymes,[6] have been shown to transfer an oxygen atom to a variety of substrates.[7] The most characteristic reaction of **2** is a nucleophilic oxidation of sulfoxides,[8] and it has been suggested that carbonyl oxides are best described as the zwitterionic form (**2a**, **2b**).



1a **1b** **1c**



2a **2b** **2c**

We became interested in the control or change of reactivities of carbonyl oxides by choosing substituents. In the present study, we have examined the structure and reactivity of α,α,α-trifluoroacetophenone oxide, a carbonyl oxide possessing a potent electron-withdrawing trifluoromethyl group. Unique chemistry of the CF_3-substituted carbonyl oxide has been revealed such as (i) an unexpected deoxygenation of sulfoxides to yield sulfides and (ii) an isomerization to the corresponding dioxirane which could epoxidize olefins electrophilically. These features are quite unique in comparison to the known chemistry of carbonyl oxides.

Results and Discussion

Formation of α,α,α-Trifluoroacetophenone Oxide 3. Carbonyl oxides can be generated from diazo compounds via the triplet route in Scheme 1; i.e., the photolysis of diazo compounds yields triplet carbenes, which react with ground-state oxygen to afford the oxides.[9] Alternatively, carbonyl oxides could be generated by the singlet oxygen oxidation of diazo precursors[10] (the singlet route in Scheme 1); in this case it is necessary to use a singlet oxygen sensitizer such as methylene blue (MB). α,α,α-Trifluoroacetophenone oxide **3** may be generated by the reaction of phenyltrifluoromethyldiazomethane **4** and singlet oxygen (the singlet route). Thus, irradiation (>400 nm) of oxygen-saturated solution of **4** (8 mM) and MB (0.24 mM) in acetonitrile at ca. 20 °C afforded over 90% yield of the corresponding ketone,

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

[1] Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed., 1984; Vol. 2, Chap. 11.

[2] Houk, K. N.; Yamaguchi, K. In *1,3-dipolar Cycloaddition Chemistry*; Padwa, A., Ed., 1984, Vol. 2, Chap. 13.

[3] Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978, Vol. I; 1982, Vol. II.

[4] (a) Ishikawa, S; Tsuji, S; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 4282. (b) Ishikawa, S; Nojima, T; Sawaki, Y. *J. Chem. Soc., Perkin Trans. 2* **1996**, 127.

[5] Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335, and references cited therein.

[6] Hamilton, G. A. In *Molecular Mechanism of Oxygen Activation*; Hayashi, O., Ed; Academic Press: New York, 1974; p 405.

[7] (a) Hamilton, G. A.; Giacin, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 1584. (b) Nakamura, N.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1986**, *108*, 4671. (c) Agarwal, S. K.; Murray, R. W. *Photochem. Photobiol.* **1982**, *35*, 31. (d) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191.

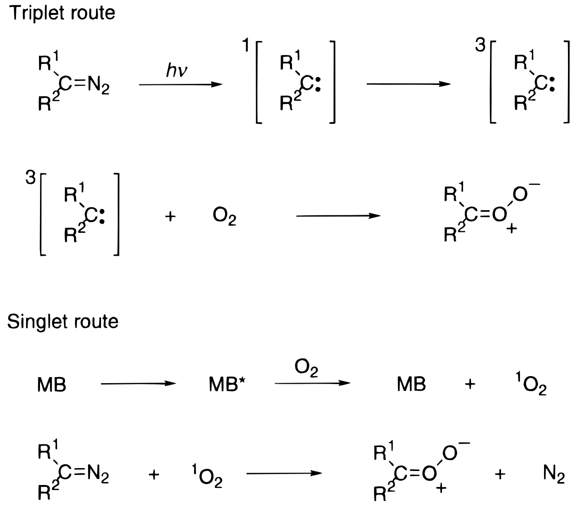
[8] (a) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832. (b) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020. (c) Adam, W.; Dürr, H.; Haas, W.; Lohray, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 101. (d) Adam, A.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202.

[9] Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391.

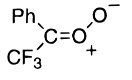
[10] (a) Higley, D. P.; Murray, R. W.; *J. Am. Chem. Soc.* **1974**, *96*, 3330. (b) Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623.

S0022-3263(96)01728-8 CCC: $14.00

Scheme 1



α,α,α-trifluoroacetophenone **5**. It is apparent that the ketone was produced by the reaction of **4** and singlet oxygen.



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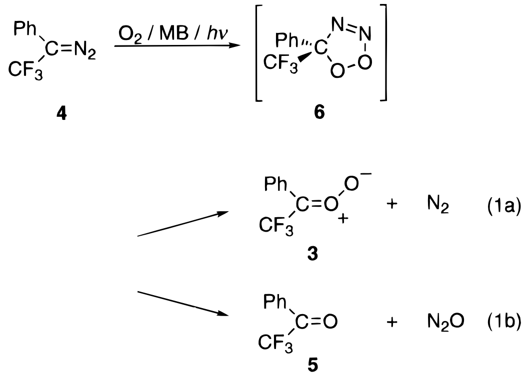
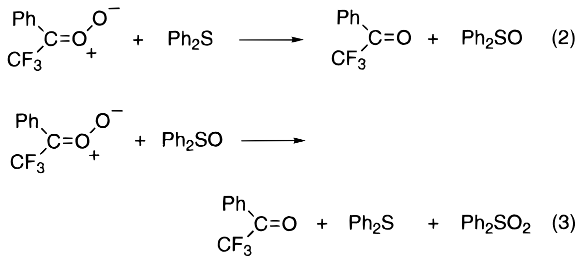
Recently, we have reported on the mechanism of singlet oxygenation of various kinds of diazo compounds.[11] It was shown that 1,2,3,4-dioxadiazole intermediates (*cf.* **6**) are formed in the $^1O_2$ oxidation of diazo compounds and yield carbonyl oxides or ketones by eliminating N_2 or N_2O, respectively, and its cycloreversion was affected by the relative stability of carbonyl oxides. Thus, the yields of carbonyl oxides in the photooxidation can be estimated from the product ratios of N_2/N_2O.



The ratio of N_2/N_2O from the reaction of **4** and singlet oxygen was determined to be 0.70, which means the formation of carbonyl oxide **3** in ca. 40% yield. The 40% selectivity for carbonyl oxide formation is somewhat lower in comparison to the other reported cases of alkylphenyldiazomethane in the range of 53−78% selectivities. The lower selectivity for carbonyl oxide **3** seems to suggest the instability of **3** owing to the destabilizing effect of CF_3 group.

Carbonyl oxide **3** may be also generated by the reaction of ground-state molecular oxygen and carbene intermediates (the triplet route). However, the direct photolysis of **4** in oxygen-saturated acetonitrile or benzene did not yield a detectable amount of **5** but a complex mixture of products by reaction with solvents. Thus, we used Freon-113 as the solvent in the direct photolysis of **4** since the longest carbene lifetime was recorded in this solvent.[12] Direct irradiation with a 300 W medium-pressure Hg lump on the oxygen-saturated solution of **4** (8 mM) in Freon-113 afforded over 90% yield of **5**, suggesting the formation of carbonyl oxide.

Reaction of 3 with Sulfides and Sulfoxides. As mentioned in the introduction, carbonyl oxides are shown to transfer an oxygen atom to a variety of substrates.[7] For instance, the oxides react with sulfides[7d] and sulfoxides,[8] affording corresponding sulfoxides and sulfones, respectively. Carbonyl oxides are known to oxidize sulfoxides nucleophilically, while they act as an electrophilic oxidant in the oxidation of sulfides. The reactivity of carbonyl oxide **3** was examined by trapping experiments with sulfides and sulfoxides.[13] Irradiation (>400 nm) on oxygen-saturated solution of 5.5 mM **4**, 0.1 mM *meso*-tetraphenylporphine (TPP), and 0.1 M diphenyl sulfide (Ph_2S) in acetonitrile−dichloromethane (3:1) afforded over 90% yield of ketone **5** together with 16.0% yield of diphenyl sulfoxide (Ph_2SO) as an oxygen transfer product (eq 2). To our surprise, the major product from the photooxidation of **4** in the presence of 0.1 M Ph_2SO was not the oxygen-transferred diphenyl sulfone (Ph_2SO_2) but the deoxygenated diphenyl sulfide (Ph_2S), the yields being 4.2 and 28.7%, respectively (eq 3). Control experiments indicated that both diazo compound **4** and singlet oxygen are necessary for this unexpected deoxygenation and that Ph_2S and Ph_2SO were unreactive toward singlet oxygen under the same conditions. These facts clearly suggest the involvement of carbonyl oxide **3** in the reaction of sulfides and sulfoxides as shown in eqs 2 and 3.



Substituent effects for substituted diphenyl sulfoxides were examined to clarify the nature of the deoxygenation and are summarized in Table 1. It is interesting to note that the resulting Hammett's ρ-value vs σ were shown to be negative for both sulfide and sulfone formations, −0.74 ($r = 0.95$) and −0.64 ($r = 0.80$), respectively. Thus, carbonyl oxide **3** is shown to exhibit an electrophilic character in the reaction with sulfoxides, probably due to the potent electron-withdrawing power of CF_3. This feature is in sharp contrast to the case of other carbonyl oxides which nucleophilically transfer oxygen to sulfoxides ($\rho = +0.26$ vs σ ($r = 0.99$) in the case of fluorenone oxide).[8a] The data in Table 1 also involves a negative ρ-value of −0.84 vs σ ($r = 0.99$) for the oxidation of

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[11] Nojima, T.; Ishiguro, K.; Sawaki, Y. *Chem. Lett.* **1995**, 545.

[12] (a) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227. (b) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813.

[13] A preliminary results on the reaction with sulfoxides are reported: Ishiguro, K.; Hirano, Y.; Sawaki, Y. *Tetrahedron Lett.* **1987**, *28*, 6201.

diphenyl sulfides to sulfoxides; similar substituent effects have been reported for other carbonyl oxides.[7d,8a]

Relative reactivity of carbonyl oxide **3** toward sulfides and sulfoxides was examined by competitive reaction using a mixture of Ph_2S and (p-$MeC_6H_4)_2SO$.[14] The resulted reactivity of Ph_2S:Ph_2SO = 1:1.64 indicates that the carbonyl oxide **3** is more electrophilic than common carbonyl oxides (typically, Ph_2S:Ph_2SO = 1:16.7 for fluorenone oxide[8a]) but the electrophilicity of **3** is not so strong as that of ozone (Ph_2S:Ph_2SO = 1:0.08[4a]).

In order to get more information about the reactivity of carbonyl oxide **3**, the effect of concentrations of trapping agent Ph_2SO was determined in detail. The resulting yields of Ph_2S and Ph_2SO_2 are plotted against the sulfoxide concentrations as shown in Figure 1A. The combined yields of Ph_2S and Ph_2SO_2 increased as the increasing concentration of trapping substrate and the extrapolated yield at $[Ph_2SO] = \infty$ was ca. 40%. This is in good agreement with the prediction of 40% carbonyl oxide formation as estimated from the N_2/N_2O ratio.

As an another interesting point, the dramatic change of product ratios of Ph_2SO_2 and Ph_2S was observed as shown in Figure 1B. The major reaction at the lower concentration of Ph_2SO is the O-transfer to the sulfoxide, while the deoxygenation is predominant at higher concentration. This point will be discussed later.

Mechanism of Deoxygenation of Sulfoxides. The deoxygenation of sulfoxides by carbonyl oxide **3** is surely an unexpected reaction. A possible scheme for this deoxygenation involves, as outlined in Scheme 2, the formation of persulfoxide intermediates, which are known to be formed in the reaction of sulfides and singlet oxygen and easily lose O_2.[15] The mechanisms as shown in Scheme 2 were examined by two experiments as follows:

(i) It is known that $^1O_2$ oxidation of benzyl phenyl sulfide results in the characteristic C−S cleavage, via persulfoxide intermediates, affording benzaldehyde (eq 4).[16] We examined the reaction of carbonyl oxide **3** with benzyl phenyl sulfoxide in polar or nonpolar solvent. As shown in Figure 2, a considerable amount of benzaldehyde as well as the corresponding sulfide and sulfone were formed in both solvents. The product ratios of aldehyde/sulfide in acetonitrile were higher than that in benzene, reflecting the stability of persulfoxides. That is, in polar solvent, persulfoxides are stable enough to proceed the abstraction of α-proton leading to the C−S cleavage (eq 4a), while they are so unstable in nonpolar solvent that the deoxygenation occurs predominantly (eq 4b).

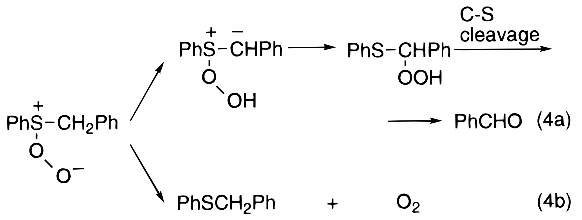

Table 1. Relative Reactivities of Substituted Diphenyl Sulfides and Sulfoxides in the Photooxidation of Phenyl(trifluoromethyl)diazomethane (4)

	relative reactivity[a]		
	additive: Ar_2S	additive: Ar_2SO	
Ar	product: Ar_2SO	product: Ar_2S	product: Ar_2SO_2
p-$MeOC_6H_4$	3.03	3.65	1.13
p-MeC_6H_4	2.61	1.68	0.44
C_6H_5	(1.00)	(1.00)	0.20
p-ClC_6H_4	0.54	0.65	0.26
ρ[b]	−0.84	−0.74	−0.64

[a] Relative reactivities toward carbonyl oxide **3** by competitive reactions. Initial concentrations; 7.0 mM **4**, 0.1 mM TPP, 0.1 M each of sulfides or sulfoxides in $MeCN-CH_2Cl_2$ (3:1); solutions were irradiated at >400 nm under oxygen at 20 °C for 30 min, and products were determined by GLC. [b] The Hammett ρ-value vs σ.

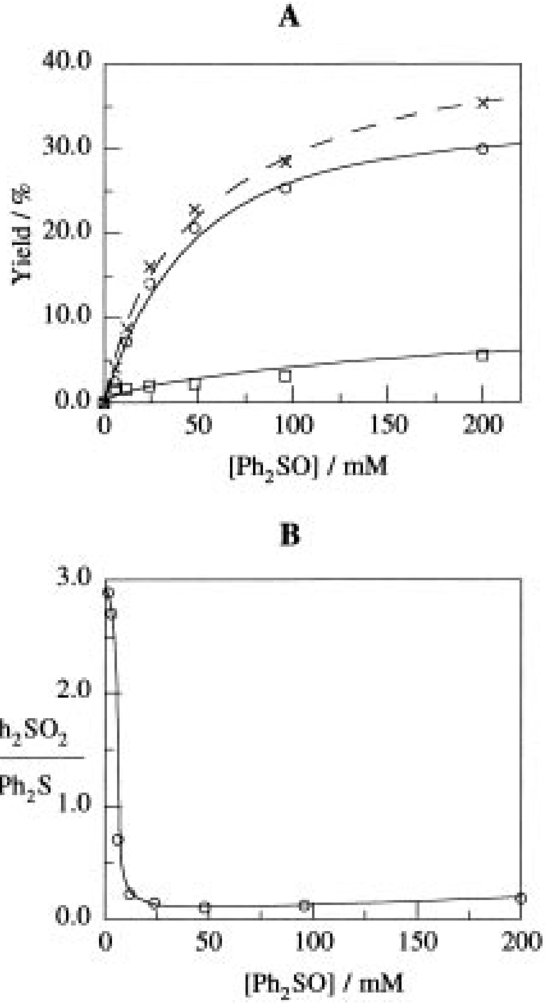

Figure 1. Trapping by Ph_2SO in the photooxidation of **4** in acetonitrile using MB sensitizer. Plots of % yields of Ph_2S (open circle), Ph_2SO_2 (open square), and ($Ph_2S + Ph_2SO_2$) (cross) (A) and plot of Ph_2SO_2/Ph_2S (B) vs the concentration of Ph_2SO. For initial concentrations see note *a* in Table 2. Products were determined by GLC, and % yields are based on **4**.

The aldehyde may be also generated by the secondary reaction of produced $PhSCH_2Ph$ with singlet oxygen during the photooxidation of **4**. In order to check such possibility, the photooxidation of **4** (2.5 mM) was carried out in the copresence of $PhSOCH_2Ph$ (35 mM),

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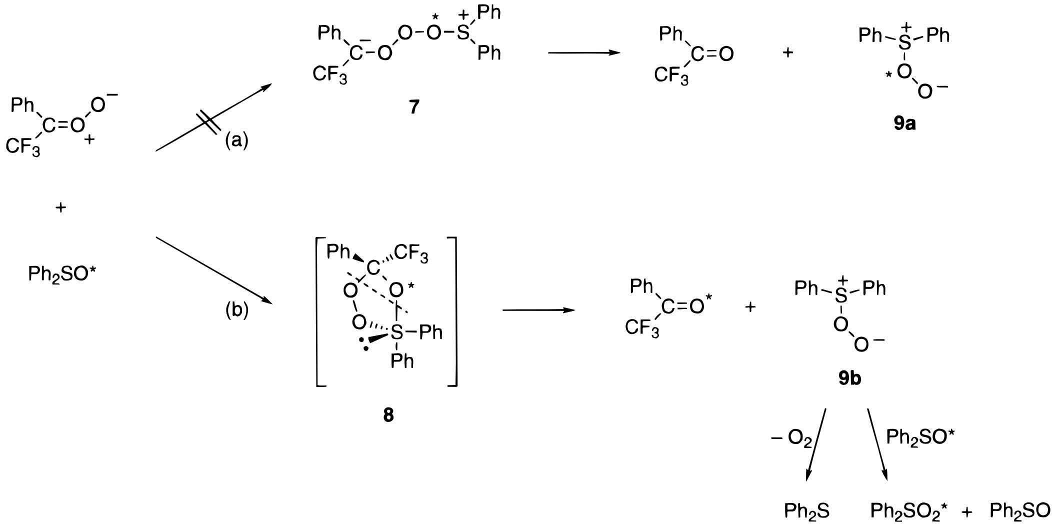
[14] The yields of products were Ph_2SO (8.66%), (p-$MeC_6H_4)_2S$ (21.7%), and (p-$MeC_6H_4)_2SO_2$ (2.22%) for the photooxidation of **4** (6.7 mM) in the copresence of 0.1 M Ph_2S and (p-$MeC_6H_4)_2SO$ in acetonitrile, revealing the relative reactivity of Ph_2S: (p-$MeC_6H_4)_2SO$ = 1:2.76. After correction of selectivity for Ph_2SO vs (p-$MeC_6H_4)_2SO$ in Table 1, the relative reactivity toward Ph_2S vs Ph_2SO was determined to 1:1.64.

[15] Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

[16] (a) Corey, E. J.; Ouannès, C. *Tetrahedron Lett.* **1976**, *17*, 4263. (b) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154. (c) Ando, W.; Ito, K.; Takata, T. *Tetrahedron Lett.* **1982**, *23*, 3909.

Scheme 2



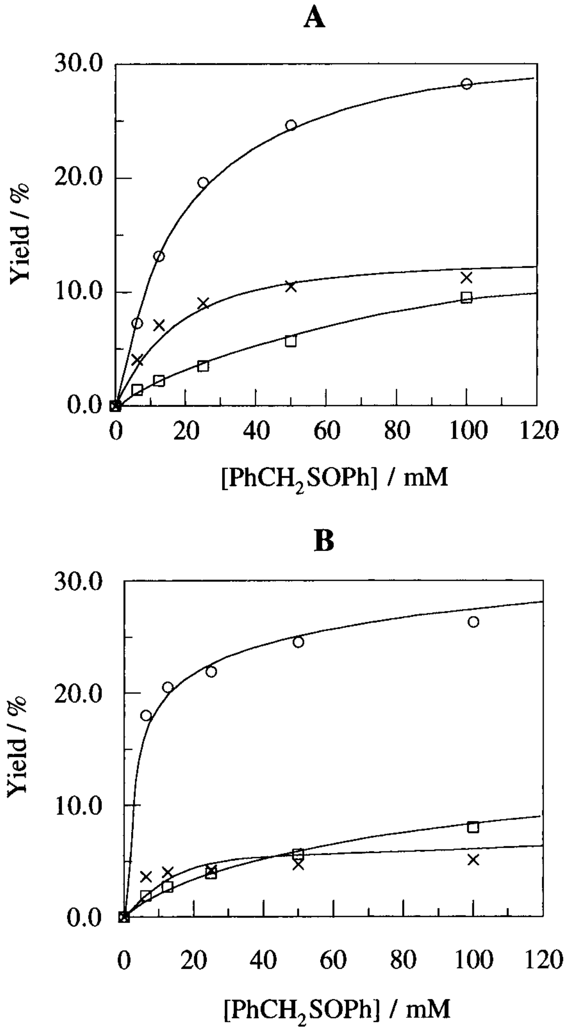
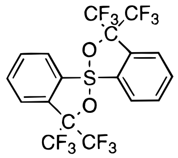


Figure 2. Plots of yields of $PhCH_2SPh$ (open circle), $PhCH_2SO_2Ph$ (open square), and PhCHO (cross) vs the concentrations of $PhCH_2SOPh$ added in the photooxidation of **4** in acetonitrile (A) containing MB or in benzene (B) containing TPP. Products were determined by GLC, and % yields are based on **4**. See note *a* in Table 2 for conditions.

$PhSCH_2C_6H_4CH_3$ (1 mM), and MB (0.2 mM) in acetonitrile. The products of the photooxidation were $PhSCH_2Ph$ (29.3%), $PhSO_2CH_2Ph$ (6.9%), PhCHO (5.5%), and only a small amount of $CH_3C_6H_4CHO$ (1.4%).[17] This control experiment indicated that the major amount of aldehyde was formed via the reaction of $PhSOCH_2Ph$ with carbonyl oxide **3** during the photooxidation of **4**. All of these facts suggested the intermediacy of persulfoxides in the deoxygenation of sulfoxides.

(ii) The fate of oxygen atom in sulfoxides during the deoxygenation was examined by a tracer study using ^{18}O-labeled Ph_2SO (97.8% ^{18}O). As shown in Scheme 2, the persulfoxides **9** may be formed via two routes, via a linear trioxide **7** (path a) or a cyclic sulfurane **8** (path b). According to the former mechanism, the sulfoxide ^{18}O is to be exhausted as molecular oxygen, while the labeled oxygen should be transferred to ketone oxygen in the latter case. The observed ^{18}O-content in ketone **5** was 15.4 ± 0.1% showing that the oxygen atom in Ph_2SO is actually taken into the ketone during the deoxygenation. Moreover, the ^{18}O-content was in agreement with the combined yields (16.5%) of Ph_2S (13.8%) and Ph_2SO_2 (2.7%). These results clearly showed that the persulfoxide was formed via the cyclic sulfurane intermediate.

In the reaction of carbonyl oxide **3** with sulfoxides, the resulting sulfides seem to be formed by the deoxygenation of persulfoxides via cyclic sulfurane intermediate **8**. Although most of sulfuranes are not stable and quite reactive toward trace amounts of water, some isolable sulfuranes, such as **10**, are known in which the negative charge in apical ligands is stabilized by electron-withdrawing CF_3 group.[18] Hence, the formation of cyclic sulfurane intermediate **8** similarly stabilized by CF_3 in the present deoxygenation is not unreasonable.



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The well-known nucleophilic reactivity of carbonyl oxides is understood by the formation of adduct **11** leading to sulfone formation as shown in eq 5. In the

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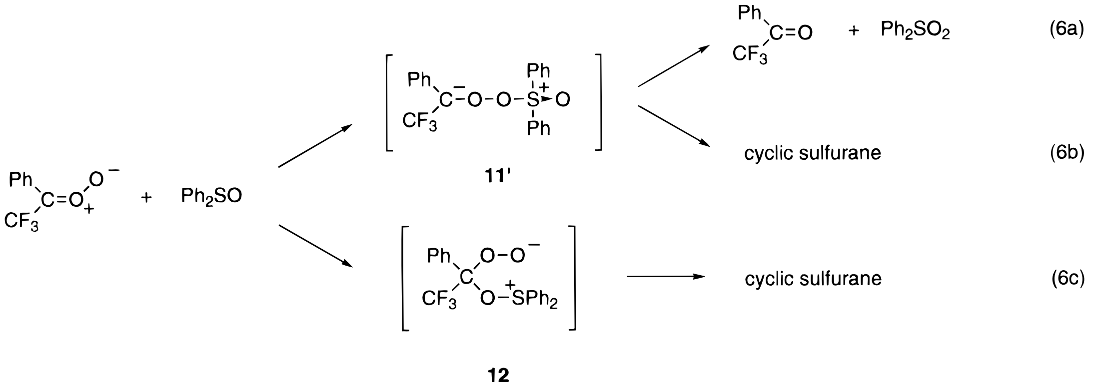
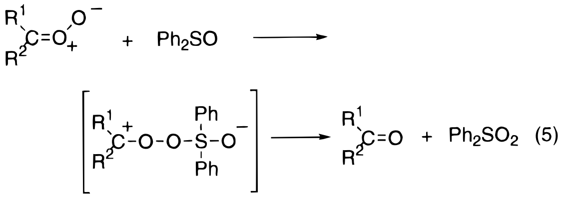
(17) % Yields are based on **4** consumed.

(18) Martin, J. C.; Perozzi, E. F. *Science* **1976**, *191*, 154.

Scheme 3



present case (R^1 = Ph, R^2 = CF_3), the major reaction is the deoxygenation via cyclic sulfurane intermediates. The



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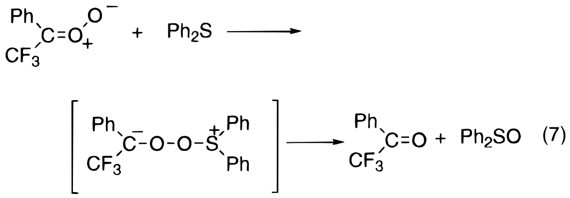
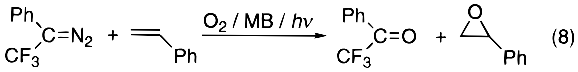
resulting negative Hammett's ρ-value indicates that the carbonyl oxide can electrophilically react with sulfoxides as in the case of ozone when a strongly electron-withdrawing group substituted. Such a biphilicity has been documented for a variety of 1,3-dipolar species.[19] If the terminal oxygen in carbonyl oxide is to add to the sulfoxides, the O−O cleavage of the resulting adduct **11′** to yield sulfones (eq 6a) would be facile, and hence it is difficult to consider that cyclic sulfurane is predominantly formed from adduct **11′** (eq 6b). A more acceptable picture for the formation of cyclic sulfuranes would be the electrophilic attack of carbon atom of the carbonyl oxide to sulfoxide to yield **12**, which is facilely cyclized to form sulfurane **8** as shown in eq 6c.

On the other hand, the negative Hammett's ρ-value for the oxidation of sulfides to sulfoxides indicates that the carbonyl oxide oxygen would electrophilically attack toward the sulfur atom of sulfides (eq 7).



Reaction with Olefins. It is interesting to note the concentration effect of diphenyl sulfoxides on the ratio of sulfides and sulfones as shown in Figure 1B; the oxidation of Ph_2SO is predominant at lower concentrations of Ph_2SO, while the major reaction at higher concentration is the deoxygenation of Ph_2SO. This result implies the presence of two different intermediates, which was examined using olefins as an another trapping agent.

The irradiation (>400 nm) of oxygen-saturated solution of **4** (7.7 mM), 0.24 mM MB, and 100 mM styrene in acetonitrile afforded the corresponding ketone **5** (>90%) and styrene oxide (9.1%) (eq 8); no C−C cleaved products such as benzaldehyde were formed. The substituent



effect for the epoxidation was studied by competitive method, relative rates being 6.40, 2.74, 1.00, and 0.46 for styrenes with substituents *p*-MeO, *p*-Me, H, and *m*-Cl, respectively. The ρ-value for substituted styrenes vs σ was negative value of −1.66, showing that the epoxidation occurred electrophilically (Figure 3). Under the same conditions, *trans*-stilbene afforded solely *trans*-stilbene oxide and *cis*-stilbene gave *cis*-stilbene oxide predominantly, the cis/trans ratio being 85/15 as listed as run 5 in Table 2. We assumed that the stereospecific epoxidation proceeded as the major reaction and that the loss of stereoselectivity might be due to a side reaction.

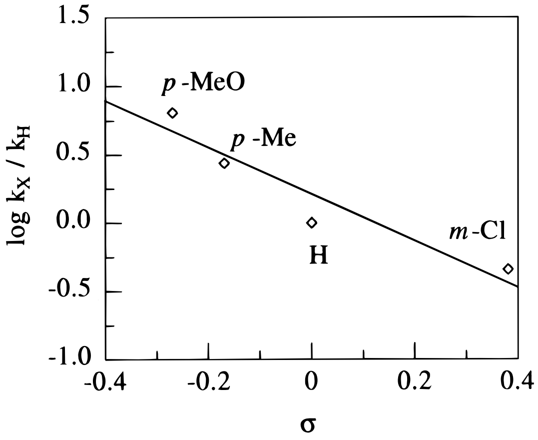


Figure 3. Hammett plot for the epoxidation of substituted styrenes in the photooxidation with **4** in acetonitrile containing MB. See text for the conditions.

The characteristics of the cooxidation of olefins are summarized as: (i) the high selectivity for the epoxide formation, (ii) the preference for electron-rich olefins, and (iii) the high conservation of olefin stereochemistry. It is interesting that these features are contrasted with those of known carbonyl oxides, which is more reactive toward electron-deficient olefins reflecting their nucleophilic nature.[20] Moreover, the cooxidation of styrenes during the photooxidation of diazofluorene afforded PhCHO (7.7%) and styrene oxide (2.7%), suggesting that

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[19] Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed., 1984; Vol. 1, Chap, 1.

[20] Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 7681.

Table 2. Products from the Photooxidation of Diazomethane 4 in the Presence of Additives under Oxygen[a]

run no.	additive	solvent[b]	products (%)[c]
1	$PhCH_2SOPh$ (100 mM)	AN	$PhCH_2SPh$ (28.2), $PhCH_2SO_2Ph$ (9.5), PhCHO (11.2)
2	$PhCH_2SOPh$ (100 mM)	benzene	$PhCH_2SPh$ (26.3), $PhCH_2SO_2Ph$ (8.0), PhCHO (5.1)
3	styrene (100 mM)	AN	styrene oxide (10.4)
4	*trans*-stilbene (40 mM)	AN	*trans*-stilbene oxide (7.0)
5[d]	*cis*-stilbene (48 mM)	AN	*cis*-stilbene oxide (9.0) *trans*-stilbene oxide (1.5)

[a] Irradiated at >400 nm for 30 min at 20 °C. Initial concentrations: ~3 mM **4** for runs 1 and 2, ~10 mM **4** for runs 3–5; sensitizers: 0.2 mM MB in MeCN and 0.2 mM TPP in benzene. [b] AN: acetonitrile. [c] % Yields based on **4** consumed. [d] Irradiated at >560 nm to prevent the isomerization of *cis*-stilbene to *trans*-stilbene.

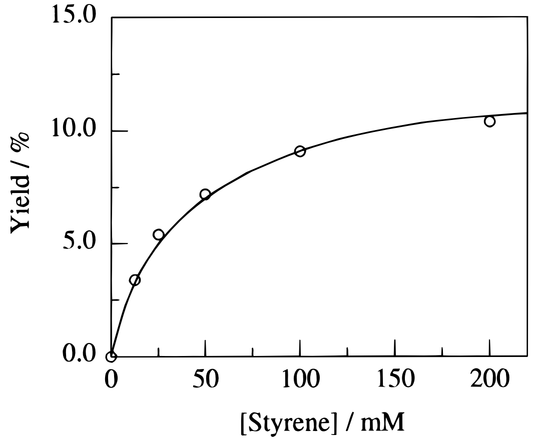

Figure 4. Plot of styrene oxide yields vs the concentration of styrene for the photooxidation of **4** in acetonitrile containing MB.

the major reaction was the C–C cleavage of olefins.[8a] Murray et al. reported that the oxygen transfer from carbonyl oxides to olefins did occur, but a significantly lower transmission of stereochemistry in epoxidation by photochemically produced carbonyl oxides compared to that formed with thermally generated singlet oxygen (from $(PhO)_3PO_3$).[21] Although actual oxidants in these reactions are not characterized, the reactivity for olefins observed in the present case is quite specific and contrasted to previous examples.

Dioxirane as a Second Intermediate. As mentioned above, the reactivities for olefins observed for the intermediate in the present photooxidation of **4** are quite contrasted to those of reported carbonyl oxides. This suggests an involvement of different type active oxygen species. Further evidence for the present of two intermediates will be shown as follows:

Trapping efficiencies were determined for the various concentrations of styrene during the photooxidation of **4**. The epoxide yields increased with the increasing concentrations of styrene as shown in Figure 4, but the maximum yield was only 10%, based on **4**, with the large excess amount of styrene. Under the same conditions, the yield of carbonyl oxide **3** formed was estimated to be as much as 40%, as mentioned earlier. The disagreement between the yield of **3** and that of epoxide might suggest that styrenes trapped another intermediate generated in about 10% during the photooxidation.

Intervention of two types active oxygen species was also supported by the competitive oxidation of styrene and diphenyl sulfoxide. The resulting product distributions were strongly depended on the concentration of diphenyl sulfoxide as shown in Figure 5. In the presence

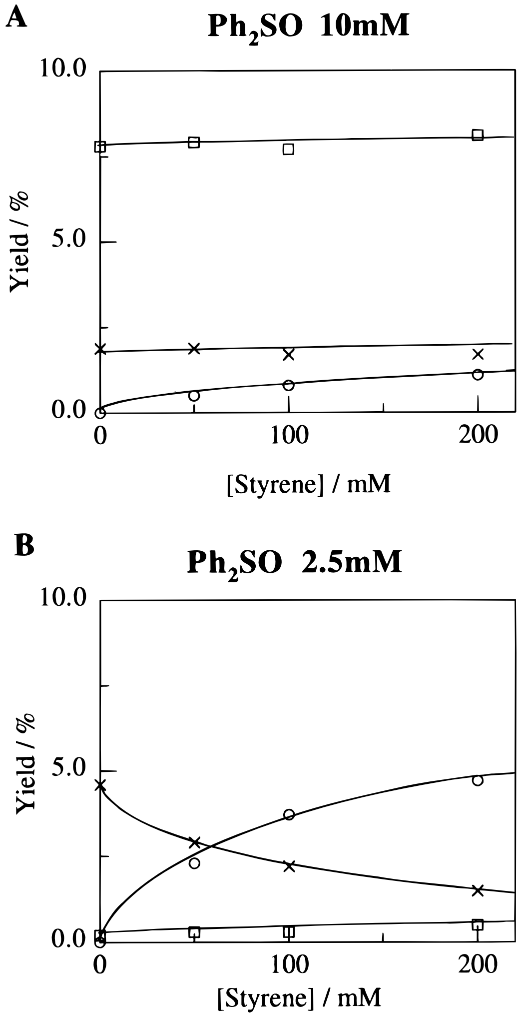

Figure 5. Competitive reactions of sulfoxides and styrene: Plots of % yields of Ph_2S (open square), Ph_2SO_2 (cross), and styrene oxide (open circle) vs styrene concentrations for the photooxidation of **4** with 10 mM (A) and 2.5 mM (B) Ph_2SO in acetonitrile containing MB.

of 10 mM Ph_2SO, the formation of styrene oxide was significantly suppressed, and the major reaction was deoxygenation of sulfoxide (Figure 5A). At the lower concentration (i.e., 2.5 mM) of Ph_2SO, however, the deoxygenation of sulfoxide became only a minor reaction, and the predominant sulfone formation was competitive with the epoxidation, since the yields of sulfone were decreased with increasing amount of styrene oxide (Figure 5B). These results show that the deoxygenation of Ph_2SO was not affected by the addition of a large excess of styrene, while the epoxidation of styrene was inhibited by the addition of only a small amount of Ph_2SO. These results indicate that, while carbonyl oxide **3** leads to the deoxygenation of Ph_2SO as mentioned

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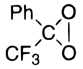
previously, styrene is oxidized by an another intermediate, formed from **3**, which also oxidizes Ph_2SO to Ph_2SO_2.

From above results, the presence of two intermediates in the photooxidation is evident. Considering these experimental results, (a) the presence of electrophilic intermediate formed via carbonyl oxide, (b) stereospecificity in the epoxidation, (c) a negative ρ-value for substituted styrene, a dioxirane may be considered as the second intermediate. It is well-known that dioxiranes oxidize olefins stereospecifically[22] and the present ρ-value of -1.66 for substituted styrenes is quite close to the reported value of -1.53 for dimethyldioxiranes.[23] The limiting trapped yield of 10% for styrene oxide in acetonitrile indicates the formation of dioxirane **13** by 25% selectivity from carbonyl oxide **3** which was produced in 40% yield from **4** and singlet oxygen. The competitive trapping experiments with Ph_2SO and styrene may be interpreted that the initially formed carbonyl oxide **3** can isomerize to dioxirane **13** only at the lower sulfoxide concentration in such a case as shown in Figure 5B. Moreover, the dramatic change of product ratios of Ph_2SO_2 and Ph_2S as shown in Figure 1B (*vide supra*) would indicate that, when the amount of sulfoxides was not enough to trap **3**, the isomerization of carbonyl oxide to dioxirane became faster, resulting in the predominant sulfone formation. These considerations support the intervention of dioxirane intermediate **13**. Other possible cases are examined in the following.



13

First, the effect of trace amounts of water was examined since carbonyl oxides are known to be converted to hydroperoxides in protic solvents.[3] If carbonyl oxide **3** was trapped by the residual trace amounts of water, α-hydroxy hydroperoxide would be formed which might be electrophilic enough to epoxidize olefins.[24] The 10% yield of styrene oxide was, however, reduced down to only 0.4% when a large excess of water (0.2 M) was added in acetonitrile (*cf.* run 3 in Table 2). This control experiment eliminated an intervention of hydroperoxide intermediates.

Second, an electrophilic oxidant might be formed by the radical chain decomposition of diazomethanes.[25] Such a reaction was shown to proceed during the photooxidation of alkyl phenyl dizaomethanes affording alkyl benzoates. However, the attempt decomposition of **4** (9 mM) initiated by di-*tert*-butyl peroxyoxalate (3 mM), which yields t-BuO$^\bullet$ and CO_2 at 55 °C in benzene,[26] was unsuccessful under air at 55 °C for 2.5 h. Consequently, diazomethane **4** was shown not to be reactive toward the alkoxyl radical, eliminating the participation of the radical decomposition during the photooxidation.

From above results, the dioxirane intermediate **13** is the most appropriate species for the electrophilic epoxidation. The formation of dioxiranes has been reported in the gas phase ozonolysis of olefins and the photochemical cyclization of carbonyl oxides in low temperature matrices is well-known.[27] As for the photochemical isomerization, a preliminary laser flash photolysis study were carried out. It was shown that carbonyl oxide **3** ($\lambda_{max} = 380$ nm) was a short-lived species with a few hundred μs lifetime, similar to the case of Ph_2COO (i.e., $\lambda_{max} = 410$ nm, about 1 ms lifetime). Thus, it is improbable that such a short-lived intermediate could absorb light during the photooxidation of **4** with stationary light irradiation.

In solutions, the isomerization of carbonyl oxides to more stable dioxiranes does not usually proceed thermally because of the high activation energy for the isomerization[28] and the faster bimolecular reaction leading to ketones.[29] However, Sander et al. recently reported the isomerization of dimesityl ketone oxide, a sterically hindered carbonyl oxide, to corresponding dioxirane in solution at −30 °C.[30] It was also reported the isomerization of carbonyl oxide to dioxirane was observed in the ozonolysis of 1,2-dimethoxy 1,2-diphenylethene in CD_2Cl_2 at −20 °C.[31] The present results suggested the isomerization of a carbonyl oxide with a CF_3 group to the corresponding dioxirane in solution.

The Effect of a CF_3 Group. In order to understand the effect of CF_3 group on structure and energetics of carbonyl oxides, we carried out correlated *ab initio* calculations on H_2COO and CF_3HCOO. We used the density functional B3LYP[32] /6-31G** method for geometry optimization, since the optimized geometry of parent carbonyl oxide (H_2COO) with this level was in good agreement with that optimized with CCSD(T)/TZ+2P level as shown by Cremer.[28c] The calculated geometries of H_2COO were $R(OO) = 1.343$ Å, $R(CO) = 1.266$ Å, $\angle COO = 119.4°$, while those of CF_3HCOO were $R(OO) = 1.336$ Å, $R(CO) = 1.266$ Å, $\angle COO = 119.3°$ for the anti-isomer and $R(OO) = 1.336$ Å, $R(CO) = 1.270$ Å, $\angle COO = 120.1$ for the syn-isomer, respectively. Comparing the bond lengths, it is found that the substitution of H by CF_3 results in a decrease in the O−O bond strength and a slight increase in the C−O bond. Such tendency was consistent with the experimental IR spectra of Ph_2COO and $PhCF_3COO$ reported by Sander in a low temperature argon matrices in which the O−O and C−O stretching vibrations were significantly shifted by the substitution of Ph by CF_3.[33] From these results, it may be appropriate that the structure of the CF_3-substituted carbonyl oxide is formulated as biradical structure **2c** rather than zwitterionic ones (**2a**,**2b**). These theoretical and spectroscopic interpretations are consistent with the electrophilic reactivity of the carbonyl oxide **3** as revealed in the present study.

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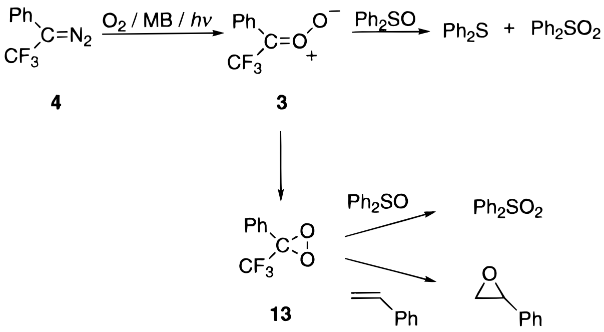
Scheme 4



Cremer et al. carried out *ab initio* calculations about the isomerization of carbonyl oxides to dioxiranes.[28a] It is reported that the conversion of parent carbonyl oxide (H_2COO) to the corresponding dioxirane is exothermic by 31.3 kcal/mol but has an activation energy of 25.0 kcal/mol (at MP2/6-31G* level). On the other hand, in the case of monofluorocarbonyl oxides, the activation energies of the isomerization to monofluorodioxirane was reduced to 17.1 and 7.9 kcal/mol (at MP2/6-31G* level), for the syn- and anti-isomers, respectively. Moreover, the same reduction of a barrier to ring closure of carbonyl oxide was reported for difluorocarbonyl oxides.[34] These dramatic effects of fluorine were explained by its π-donor property to stabilize the transition state for the isomerization. In the present case of the carbonyl oxide with the CF_3 group, however, such an acceleration is not expected.

Unfortunately, the effect of the CF_3 group on the isomerization of carbonyl oxide **3** to dioxirane has not been well understood, but solvents may play some of acceleration effect. Further detailed theoretical consideration about the isomerization of carbonyl oxide **3** is now in progress.

Conclusions

Quite a unique character of CF_3-substituted carbonyl oxide **3** has been revealed. The oxide effectively deoxidized sulfoxides affording sulfides as the main product. When the sulfoxide concentration is low, the second intermediate is formed from the oxide, which oxidizes sulfoxides to sulfones and olefins to epoxides stereospecifically as the major reaction. Dioxirane **13** is the most plausible candidate for the second intermediate. The mechanism of reactions of carbonyl oxide **3** may be summarized as in Scheme 4.

The characteristic points of reactivity of CF_3-substituted carbonyl oxide **3** are as follows: (a) The CF_3 group turns the known nucleophilic reactivity of carbonyl oxides to electrophilic as characterized by the novel deoxygenation of sulfoxides. (b) The CF_3-substituted carbonyl oxide may isomerize to dioxirane in solutions. Thus, the reactivities of carbonyl oxides can be controlled by the nature of substituents.

Experimental Section

GC-MS analyses were carried out with a Shimadzu QP-5000 mass spectrometer using a 0.2 mm × 25 m capillary column of CBP1-M50-025 (Shimadzu) and a JEOL D300 mass spectrometer using a 2.5 mm × 1 m column of Carbowax 300M, 2% on Chromosorb WAW (GL Sciences). GLC analyses were performed with a Shimadzu GC-14A and a Yanagimoto G180 gas chromatograph, using 2.5 mm × 1 m column of carbowax 300M, 2% on Chromosorb WAW (GL Sciences).

Materials. 1-Phenyl-2,2,2-trifluorodiazoethane,[35] benzyl phenyl sulfide,[36] benzyl phenyl sulfoxide,[36] 4-substituted diphenyl sulfoxide,[37] and di-*tert*-butyl peroxyoxalate[26] were prepared by the reported procedures. *p*-Methylbenzyl phenyl sulfide was prepared by the reported method for benzyl phenyl sulfide. Other reagents were of commercial sources.

Acetonitrile and benzene (Tokyo Kasei) were distilled over calcium hydride. Spectrophotometric grade Freon 113 (Nacalai) was used without further purification.

^{18}O-Labeled Diphenyl sulfoxide. A 10-mL acetonitrile solution of 0.4 mM dicyanoanthracene (DCA) and 0.12 M diphenyl sulfide in a 20-mL Pyrex reaction vessel with a stopcock was degassed by repeated freeze-pump-thaw cycles, and then 100 mL $^{18}O_2$ gas (CEA 98.75% ^{18}O) was introduced. The solution was irradiated (>350 nm) for 65 h at ca. 20 °C. ^{18}O-Labeled diphenyl sulfoxide (73.9 mg) was isolated from the reaction mixture by means of silica gel column chromatography using benzene−EtOAc as an eluent. The content of ^{18}O in the diphenyl sulfoxide was analyzed by GC-MS spectroscopy from the relative time-integrated peak areas at *m/e* 202 (M), 204 (M + 2), the latter data being corrected by abstracting the M + 2 value of natural abundance in Ph_2SO. The corrected content of ^{18}O in diphenyl sulfoxide was 97.8% ^{18}O.

***cis*-Stilbene.** A 20-mL dichloromethane of 1 g *trans*-stilbene and 0.14 g of benzil as a sensitizer in a 25-mL Pyrex tube with a rubber septum (Aldrich) was purged with oxygen. After irradiation (>400 nm, ca. 16 h at 20 °C), *cis*-stilbene was separated from the reaction mixture by silica gel column chromatography using hexane as the eluent (>99% *cis*-stilbene).

Typical Procedure of the Photooxidation. A 2.7-mL acetonitrile solution of 8 mM 1-phenyl-2,2,2-trifluorodiazoethane (**4**) and 0.24 mM methylene blue (MB) in a 25-mL Pyrex tube capped with a rubber septum (Aldrich) was purged with oxygen and irradiated with a 300 W medium pressure Hg lamp through a 5% KNO_2 filter solution (>400 nm) for 30 min at ca. 20 °C at which time **4** was completely converted to the corresponding ketone. In the case of the reaction in benzene solution, 0.2 mM *meso*-tetraphenylporphine (TPP) was used as the sensitizer. Products were determined by GLC and identified by GC-MS analysis in comparison to authentic samples.

^{18}O-Tracer Study. A 0.45-mL acetonitrile solution of 8.93 mM **4**, 0.24 mM MB, and 56.3 mM ^{18}O-labeled diphenyl sulfoxide (97.8% ^{18}O) in a 0.5-mL Pyrex tube capped with a rubber septum (Aldrich) was purged with oxygen and irradiated with a 300 W medium pressure Hg lamp through a 5% KNO_2 filter solution (>400 nm) for 30 min at ca. 20 °C. After that the content of ^{18}O in the α,α,α-trifluoroacetophenone and diphenyl sulfone formed were analyzed by GC-MS spectroscopy from the relative peak areas at *m/e* 174 (M), 176 (M + 2) and 218 (M), 220 (M + 2), 222 (M + 4), respectively. Found values: 174 (M) 84.6%, 176 (M + 2) 15.4%, 218 (M) 0%, 220 (M + 2) 66.1%, 222 (M + 4) 33.9%.

The M + 4 peak corresponds to Ph_2SO_2 of which the two ^{18}O atoms involved in the starting materials and this sulfone (M + 4) is independent of the present photooxidation. Since the total yield of Ph_2SO_2 was 4.2%, the yield of Ph_2SO_2, which was oxidized by carbonyl oxide, was 2.7%.

Determination of Gas Evolved during the Photooxidation of 4. The relative sensitivity of N_2/N_2O on the GC-MS spectroscopy at the ionizing voltage of 70 eV was determined to be 0.91 ± 0.02 from a mixture of authentic N_2 and N_2O gasses of known ratio. A 2.95-mL acetonitrile solution of 5.9 mM **4** and 0.24 mM MB in a 3-mL Pyrex tube capped with a rubber septum (Aldrich) was purged with oxygen and irradiated with a 300 W medium pressure Hg lump through

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a 5% KNO_2 filter solution (>400 nm) for 30 min at ca. 20 °C at which **4** was completely converted to ketones. After irradiation, the contents of N_2 and N_2O in solution were analyzed by GC-MS spectroscopy from relative peak areas at *m*/*e* 28 (N_2) and 44 (N_2O), respectively. Small amounts of N_2 and CO_2 (*m*/*e* 44) that leaked at the injection (less than 5% of evolved gasses) were corrected for, and the analyses were repeated for several times.

Laser Flash Photolysis. A preliminary laser flash photolysis experiments were carried out on air-saturated solution of diazo compound (10^{-4} to 10^{-3} M) using a Spectron SL284G Nd:YAG laser (266 nm, ~6 ns, ~25 mJ/pulse). Experiments were carried out by flowing solution through a 10 × 5 mm^2 quartz cell in order to ensure that each laser pulse irradiated a fresh part of volume. The decay kinetics were observed by the photomultiplier tube monitoring system. The system was controlled by a PC-9801RX computer which was interfaced (GPIB) to a GOULD 4072 digital oscilloscope that was used for data acquisition.

Theoretical Calculations. *Ab initio* calculations were carried out on a DEC VENTURIS 5100 computer using Gaussian 94.[38] Density functional theory (DFT) calculation employed the B3LYP exchange correlation functional.[32] Total energies and geometry data reported in this paper are available as Supporting Information.

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Supporting Information Available: A table of total energies and geometry data reported in this paper (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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