

cross-linked catalysts are explained by slower diffusion of reactant. The cases of faster rates of reaction of benzyl chloride and of 1-bromooctane with cyanide ion in a 10% cross-linked catalyst than in a 2% cross-linked catalyst are surprising. They are probably due to a microenvironmental effect on intrinsic reactivity. With the more active benzyltri-*n*-butylphosphonium catalysts, increases in reaction rates of all three alkyl bromides with decreases in catalyst particle sizes indicate that all of the rates are controlled by intraparticle diffusion and intrinsic reactivity.

The overall effects of intraparticle diffusion on reaction rates fall into two classes. If two substrates have nearly equal diffusivities, heterogeneous catalysts reduce differences in observed rates because diffusion limits the reaction rate of the more active substrate more than that of the less reactive substrate. If two substrates have nearly equal intrinsic reactivities and different diffusivities, heterogeneous catalysts give faster reaction rates with the faster diffusing species.

### Conclusions

Mass transfer of reactant from bulk liquid to the catalyst surface is an important factor limiting rates of polymer-bound phase-transfer-catalyzed reactions of alkyl halides with aqueous sodium cyanide unless rapid mechanical stirring is used. In our exper-

iments, at least 400 rpm, and preferably  $\geq 600$  rpm, is required to make rate limitation by mass transfer negligible. With use of other reaction vessels and mixing methods, the conditions required to attain reaction rates not limited by mass transfer will vary, and control experiments will be required to establish that mixing is effective enough to avoid mass transfer control. If mass transfer limitations are overcome, most rates of reactions of alkyl halides with sodium cyanide are limited by a combination of intraparticle diffusion and the intrinsic rate at the active site. Smaller catalyst particles, lower degrees of cross-linking of the polymer, less active catalysts, and less active substrates all decrease the contribution of intraparticle diffusion to rate limitation. In this study, only the reactions of 1-bromooctane and benzyl chloride using 2% cross-linked benzyltrimethylammonium ion catalysts were controlled strictly by intrinsic reactivity.

### Experimental Section

All chemicals were reagent grade and were used without further purification. Catalyst preparations and analyses and kinetic procedures were the same as in the preceding paper.<sup>3</sup>

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## Reactivity of Carbonyl Oxides. Characteristic Nucleophilic Oxygen Atom Transfer from $R_2COO$ beside Electrophilic and Radical Reactions<sup>1a</sup>

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**Abstract:** According to a MINDO/3 calculation, carbonyl oxide  $H_2COO$  has a large contribution of zwitterionic structure **1a**, which is not altered by phenyl substituent. The dye-sensitized photooxidation of diazomethanes in  $CH_2Cl_2$ -MeOH afforded ca. 30% yield of  $\alpha$ -methoxy hydroperoxides as product from **1a** and MeOH. Relative reactivities of various types of substrates toward the carbonyl oxide from diazofluorene and  $^1O_2$  have been determined. While benzene gave phenol in a low yield, substituted benzenes such as toluene or anisole yielded products by hydrogen atom abstraction on the side chain as a major reaction. Olefins gave a rather minor amount of epoxides; the predominant reaction was C-C cleavage or allylic hydrogen abstraction. The relative reactivity with carbonyl oxide is in the order  $Ph_2SO \gg Ph_2S > C=C > benzene$ , where  $C=C$  means  $\alpha$ -methylstyrene. This order is in sharp contrast to the case of peroxy acid,  $Ph_2S \gg Ph_2SO \gg C=C$ , or to the order with acylperoxy radical,  $C=C \gg Ph_2S, Ph_2SO$ . The above order with carbonyl oxide indicates a nucleophilic oxygen atom transfer as a characteristic reaction; this was clearly shown by the positive  $\rho$  value of +0.26 for substituted diphenyl sulfoxides. The reactivities of various substrates revealed that another characteristic reaction is hydrogen atom abstraction as a radical, and carbonyl oxides could be regarded as a rather poor electrophilic O-transfer agent. These features may be understood by representing carbonyl oxides as a resonance hybrid of  $R_2C=O^+-O^-$  (**1a**) and  $R_2\dot{C}-O-\dot{O}$  (**1c**).

Oxygen-atom transfer reactions are of current interest as a model of monooxygenase enzymes.<sup>2</sup> Much attention has been concentrated on the reactivity of carbonyl oxides,<sup>3</sup> which are believed to be formed in the ozonolysis of alkenes<sup>3</sup> and alkynes<sup>4</sup> or in the direct<sup>5</sup> or sensitized<sup>6</sup> photooxidation of diazo compounds.

Carbonyl oxides can transfer oxygen atom to alkanes,<sup>7</sup> olefins,<sup>3b,4,8</sup> sulfides,<sup>9</sup> sulfoxides,<sup>9</sup> and aromatic rings.<sup>10</sup> They are also believed to be intermediates effecting the Baeyer-Villiger reaction in the decomposition of furan endoperoxides.<sup>11</sup> Recently, a metal ion coordinated carbonyl oxide has been reported to lead to an effective epoxidation of olefins.<sup>12</sup>

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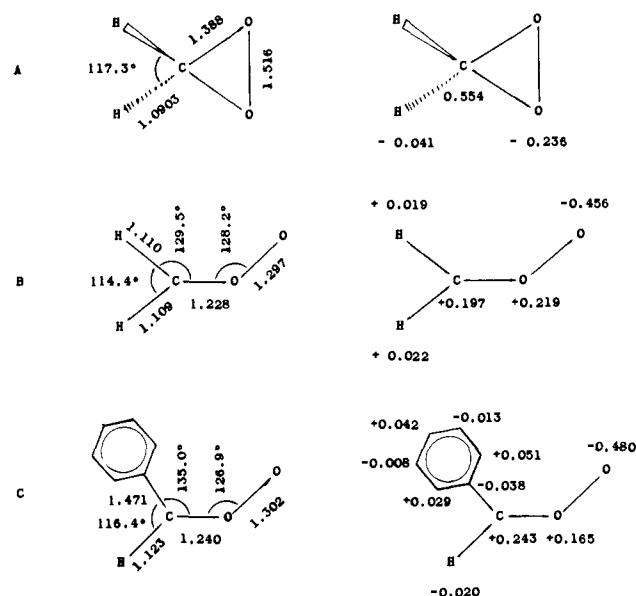
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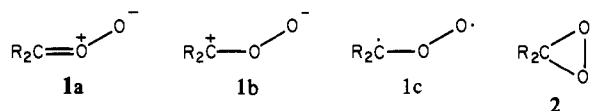


**Figure 1.** Geometric parameters (left) and charge densities (right). Bond length is in angstroms and bond angle is in degrees. Parameters for dioxirane A are observed values (ref 16). Other parameters are optimized values by the MINDO/3 method; the geometric parameters for the phenyl group are not shown.

In relation to the radical epoxidation with acylperoxy radical  $RC(=O)OO\cdot$ , formed in the photooxidation of  $\alpha$ -diketones<sup>13</sup> or benzoin, <sup>14</sup> we were interested in the reactivity of carbonyl oxides. Although many types of reactions have been reported, the reactivity of carbonyl oxides seems not to be understood well as a whole. Here, we summarize our detailed study on the structure and reactivity of carbonyl oxides from diazomethanes and singlet oxygen. Carbonyl oxides are calculated by the MINDO/3 method to possess zwitterionic structure **1a**, and are actually trapped by methanol to give  $\alpha$ -methoxy hydroperoxides. Carbonyl oxides act as effective nucleophilic oxygen-atom transfer agents but are rather mild or poor reagents as electrophilic oxenoids or as radical oxygen-atom transfer agents.

## Results and Discussion

**MO Calculations.** Carbonyl oxides (**1**) can be written as **1a-c** or sometimes as dioxirane **2**. Many MO calculations have been



done regarding the structures and stabilities of carbonyl oxides (**1**) and dioxirane (**2**); all the results have indicated that **2** is more stable than **1** by 30–40 kcal/mol.<sup>15</sup> In fact, parent dioxirane (**2**, R = H) has been synthesized and its structure was determined.<sup>16</sup> Although **2** was shown to be most stable, a MINDO/3 analysis indicated a quite high energy barrier (ca. 25 kcal/mol) in the isomerization from **1** to **2**.<sup>17</sup>

To estimate the charge density and substituent effect, we carried out a MINDO/3 calculation on carbonyl oxides. The optimized structures and charge densities are shown in Figure 1. The results on formaldehyde oxide (**1**, R = H) are close but not identical with the values by Hull;<sup>17</sup> e.g., B in Figure 1 is less stable than A by 34.1 kcal/mol, while the reported energy difference is 33.7

Table I. Orbital Energy of Carbonyl Oxide and Dioxirane by the MINDO/3 Method

	geometry in Figure 1	energy, eV	
		HOMO	LUMO
dioxirane	A	-11.330	1.370
carbonyl oxide	B	-9.732 <sup>a</sup>	0.363 <sup>b</sup>

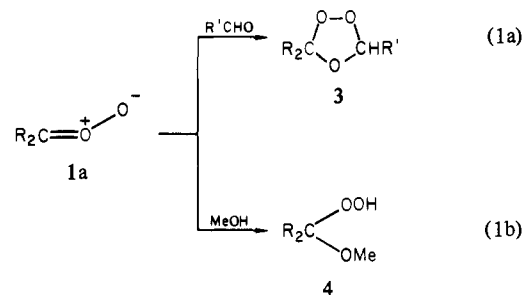
<sup>a</sup>  $\pi$ -AO coefficients for C-O <sub>$\alpha$</sub> -O <sub>$\beta$</sub>  are -0.5363, -0.2375, and +0.8099, respectively. <sup>b</sup>  $\pi$ -AO coefficients for C-O <sub>$\alpha$</sub> -O <sub>$\beta$</sub>  are -0.7570, +0.5597, and -0.3372.

kcal/mol.<sup>18</sup> The C-O bond length (1.228 Å) of B is very close to that of the C=O double bond ( $d_{C=O} = 1.24$  Å) rather than ordinal single bond ( $d_{C-O} = 1.44$  Å). The O-O bond distance (1.297 Å) is close to ozone (1.278 Å)<sup>19a</sup> or HOO $\cdot$  (1.30 Å)<sup>19b</sup> rather than oxygen (1.207 Å)<sup>19a</sup> or H<sub>2</sub>O<sub>2</sub> (1.475 Å).<sup>20</sup> The  $\pi$ -bond order of C-O <sub>$\alpha$</sub>  is as high as 0.847 and the charge densities of C-O <sub>$\alpha$</sub> -O <sub>$\beta$</sub>  (see B in Figure 1) are +0.197, +0.219, and -0.456, respectively; the  $\pi$ -bond order and charge density clearly suggest the importance of zwitterionic structure **1a**. These values do not change significantly by introducing the phenyl group (see C in Figure 1), revealing the unimportance of substituents on H<sub>2</sub>COO.

Table I lists orbital energies of dioxirane A and carbonyl oxide B in Figure 1. The ionization potential of B (i.e., 9.73 eV) is much lower than that of A; i.e., B may be a much stronger nucleophile than A. The energy of LUMO of B is also lower by ca. 1 eV than that of A; in other words, the electron affinity of B is much higher. These results show that the reactivity of dipolar carbonyl oxide **1a** is much higher both in nucleophilic and electrophilic reactions.

Although the present MINDO/3 analysis predicts the zwitterionic structure **1a** to be more stable than **1b**<sup>21</sup> or **1c**,<sup>22</sup> many rigorous ab initio calculations suggest that singlet diradical structure is considerably more stable than the dipolar **1a**.<sup>15a,b</sup> Moreover, Harding and Goddard suggested that the relative stability may be changed by substituents or solvents.<sup>15b</sup> Hence, it is interesting to study systematically the reactivity of carbonyl oxide toward various types of substrates and to compare them with these MO estimations.

**Formation and Trapping of Carbonyl Oxides.** The formation of carbonyl oxides in the ozonolysis of olefins<sup>3</sup> and alkynes<sup>4</sup> is known, but these systems are not appropriate for the study on reactivity of carbonyl oxides because of the possible involvement of some other peroxidic species.<sup>4</sup> The most clean and convenient method for carbonyl oxide generation is probably the reaction of diazo compounds with singlet oxygen.<sup>6</sup> A good evidence for its generation is the formation of ozonides (**3**) (eq 1a) as reported for the dye-sensitized photooxidation of diazomethanes in aldehydes.<sup>6</sup>



(18) Moreover, the optimized structure B is somewhat different from the reported one; e.g., the reported C-O and O-O bond lengths are 1.252 and 1.268 Å, respectively.<sup>17</sup> The reason for the discrepancy is not clear, but our calculation was optimized according to the reported method: J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).

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(21) Assuming  $d_{C-O} = 1.41$  Å for **1b** (R = H), the energy of **1b** was approximately 1.05 eV higher than that of the optimized B in Figure 1.

(22) The triplet energy of structure B (Figure 1) by UHF MINDO/3 calculation was 1.21 eV higher than the ground state. This means that diradical structure **1c** is more unstable than **1a**.

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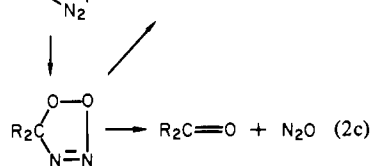
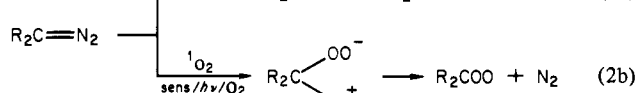
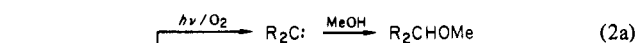
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Table II. Photooxidation of Diazo Compounds in  $\text{CH}_2\text{Cl}_2$ -MeOH under Oxygen

diazo compd $\text{R}_2\text{C}=\text{N}_2$	conditions <sup>a</sup>	% of products <sup>b</sup>			
		$\text{R}_2\text{-CHOMe}$	4	$\text{R}_2\text{-C=O}$	others
$\text{Ph}_2\text{C}=\text{N}_2$	Pyrex/20 °C/ 30 min	73	13	13	$\text{PhCO}_2\text{Me}$ (1%)
	MB/20 °C/5 min	9	24	66	
	RB/0 °C/10 min	10	29	60	
diazofluorene	RB/0 °C/10 min <sup>c</sup>	0	28	72	
	Pyrex/0 °C/ 30 min	62	1	10	fluorene (9%)
	RB/0 °C/5 min	3	34	63	

<sup>a</sup> Irradiation of 40–60 mg of diazo compound in  $\text{CH}_2\text{Cl}_2$  (20 mL)-MeOH (5 mL) with oxygen bubbling. Pyrex means the direct irradiation through Pyrex (i.e., >290 nm). The sensitized photooxidations were done by irradiating at >400 nm in the presence of 3–4 mg of Methylene Blue (MB) or Rose Bengal (RB). <sup>b</sup> Products were determined by NMR and/or GLC. <sup>c</sup> The solution of  $\text{Ph}_2\text{C}=\text{N}_2$  was slowly added dropwise during the irradiation.

Assuming that carbonyl oxides could be trapped by methanol,<sup>3a</sup> if the oxides are in the dipolar structure **1a**, we examined the photooxidation of diazo compounds in the presence of MeOH. Table II summarizes the results on the photooxidation of diphenyldiazomethane (**5**) and 9-diazofluorene (**6**). The direct irradiation (>290 nm) of diazo compound gave a methyl ether, an O-H insertion product of carbene formed (eq 2a).



On the other hand, the singlet oxygen reaction by  $\text{sens}/h\nu/\text{O}_2$  afforded 20–30% yields of  $\alpha$ -methoxy hydroperoxide (**4**) in addition to ketone (60–70% yields) and methyl ether  $\text{R}_2\text{CHOMe}$  (0–10% yields). Interestingly, the reaction of free carbene (eq 2a) became negligible when the diazo compound was added dropwise slowly during the irradiation (Table III), and the decomposition in the absence of the sensitizer was very slow (i.e., ca. 1/50). These facts clearly suggest that carbonyl oxides are produced via the  $^1\text{O}_2$  reaction of diazo compounds, supporting the scheme (eq 2b and 2c) by Murray et al.<sup>6</sup> Since the reaction of free carbenes with MeOH is very fast or nearly diffusion controlled,<sup>23</sup> its trapping by oxygen ( $\sim 0.01$  M) is quite inefficient in the presence of solvent methanol. Thus, it is apparent that carbonyl oxides are effectively (e.g., minimum 30%) produced in the reaction of the diazomethanes with  $^1\text{O}_2$ .

**Reaction of Carbonyl Oxide with Benzenes and Cyclohexane.** The reactivity of carbonyl oxide was examined with fluorenone oxide (**7**), produced from 9-diazofluorene and  $^1\text{O}_2$ , in view of the low photochemical reactivity of fluorenone,<sup>24</sup> a major reaction product. We are interested in the O-transfer reaction at ambient temperature, and hence reactions have been carried out mostly at 20 °C.

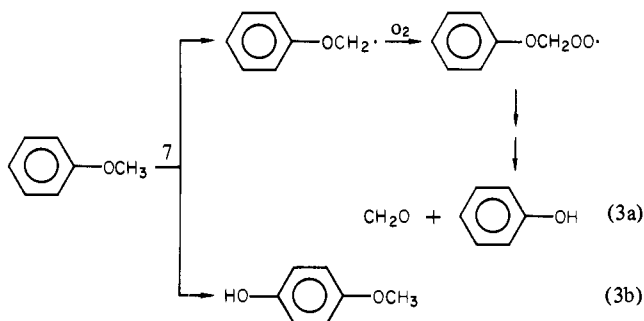
The *meso*-tetraphenylporphine (TPP)-sensitized photooxidation of **6** in aerated benzene afforded a small amount (i.e., 3.5%) of phenol; yields are always based on the diazo compound. The hydroxylation of aromatic rings is already known.<sup>10</sup> It is noteworthy that the side-chain oxidation is predominant rather than

Table III. Products in the Sensitized Photooxidation of 9-Diazofluorene (**6**)<sup>a</sup>

no.	substrate <sup>b</sup>	% of products <sup>c</sup>	
		PhOH	others <sup>c</sup>
1	benzene (solvent)	3.5	
2	5 M toluene	4.8	<i>p</i> -cresol (1.3%), PhCHO (1.8%), PhCH <sub>2</sub> OH (1%)
3	5 M cumene	0.4	PhCMe <sub>2</sub> OOH (18%)
4	anisole (solvent)	2.4	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> OH (0.43%)
5	5 M cyclohexane	1.4	C <sub>6</sub> H <sub>11</sub> OOH (11%) <sup>d</sup>
6	0.2 M PhCH=CH <sub>2</sub>	3.2	epoxide (2.7%), PhCHO (7.7%)
7	0.2 M PhMeC=CH <sub>2</sub>	2.6	epoxide (3.8%), PhCOMe (7.6%), 8 (4.7%), 9 (2.9%)
8	0.2 M PhMeC=CH <sub>2</sub> at -50 °C	1.0	epoxide (1.7%), PhCOMe (3.3%), 8 (0.4%), 9 (0.3%)
9	0.2 M cyclohexene	1.7	epoxide (2.1%), ROOH <sup>e</sup> (16%)
10	0.2 M <i>cis</i> -2-octene	1.5	epoxide (2.0%), <sup>f</sup> ROOH <sup>g</sup> (30%)
11	0.1 M Me <sub>2</sub> SO	0.9	Me <sub>2</sub> SO <sub>2</sub> (16%)
12	0.1 M Ph <sub>2</sub> SO	1.1	Ph <sub>2</sub> SO <sub>2</sub> (40%)
13	0.1 M Ph <sub>2</sub> S	2.9	Ph <sub>2</sub> SO (3%)

<sup>a</sup> Aerated solutions of ca. 1 mM diazofluorene and 0.05 mM TPP were irradiated at >400 nm for 30 min at 20 °C. <sup>b</sup> In benzene if not noted otherwise. <sup>c</sup> Products were determined by GLC and iodometric titration. Yields of fluorenone were 90–95% and not shown. <sup>d</sup> The thermolysis GLC at 220 °C gave a 1:1 mixture of cyclohexanone and cyclohexanol. <sup>e</sup> Cyclohexenyl hydroperoxide. However, a control  $^1\text{O}_2$  experiment in the absence of diazo compound resulted in a rather higher yield of products with a similar ratio. <sup>f</sup> The *cis/trans* ratio of epoxides is 2:1; the products ratio was approximately the same for the reaction at -50 °C. <sup>g</sup> Mixture of allylic hydroperoxides; their structures were not determined.

the ring hydroxylation for the cases of toluene, cumene, and anisole. That is, the formation of cumyl hydroperoxide from cumene and of benzaldehyde or benzyl alcohol from toluene clearly suggest a radical attack by carbonyl oxide. A major product from anisole is phenol, which is probably produced by the hydrogen atom abstraction on the methyl group (eq 3a). The ratio of side-chain ring attack is 2:1 for toluene and 20:1 for anisole as estimated from the product ratios in Table III.

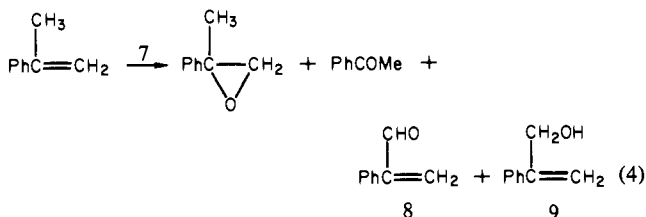


The reaction in cyclohexane gave 11% yield of cyclohexyl hydroperoxide, which was converted into a 1:1 mixture of cyclohexanol and cyclohexanone by the prolonged irradiation or the thermolysis GLC (220 °C). The latter two products were reported by direct (i.e., not sensitized) irradiation.<sup>7</sup> These facts indicate that carbonyl oxides react as a H-atom abstractor leading to the autoxidation products.

**Reaction with Olefins.** Oxygen-atom transfer from carbonyl oxides to olefins has been reported at low temperatures of -90 °C.<sup>8</sup> As shown in Table III, the reaction of **7** with styrenes afforded only a small amount (2–4%) of epoxide, the major products being from the C-C cleavage of olefin. The products from  $\alpha$ -methylstyrene involve 2-phenylacrolein (**8**) and 2-phenylallyl alcohol (**9**), which are probably produced via the radical abstraction of the allylic hydrogen. The product ratio of epoxide and acetophenone (i.e., the C-C scission product) is the same in the reaction at -50 °C, while the selectivities for **8** and **9** are substantially reduced. The two products, **8** and **9**, are also produced by the reaction with  $^1\text{O}_2$ , but the  $^1\text{O}_2$  reaction is

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much slower. The reaction of the olefin with benzophenone oxide, produced from **5** and  $^1\text{O}_2$ , resulted in a similar product ratio.

The reaction of **7** with cyclohexene also gave a low (i.e., 2%) yield of epoxide and the major product was cyclohexenyl hydroperoxide. However, a control experiment without diazo compound (i.e., the  $^1\text{O}_2$  reaction of cyclohexene) resulted in rather higher yields of products with a similar product ratio. The product was practically the same with the AIBN-initiated autoxidation of cyclohexene at 60 °C. Hence, it is not apparent whether the epoxide was the product of the direct reaction with carbonyl oxide or not.

Similarly, the reaction with *cis*-2-octene gave only a small amount of epoxide (2%). The *cis/trans* ratio of the resulting epoxide was 2:1; the same was true for the reaction at -50 °C. This ratio is different from the *trans*-dominating ratio of 1:4 by acylperoxy radical.<sup>14</sup> The reason for the large difference is not clear at present, but we feel that the epoxidation with carbonyl oxide is too inefficient. These results lead to a conclusion that carbonyl oxides are not an efficient reagent for the epoxidation of olefins, and instead lead to the C-C scission or the allylic hydrogen abstraction of olefins.

**Reaction with Sulfides and Sulfoxides.** Ando et al.<sup>9</sup> found that carbonyl oxides can transfer oxygen atom to sulfur compounds and dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) is much more reactive than diphenyl sulfide. We ascertained this tendency;  $\text{Ph}_2\text{SO}$  was much more reactive than  $\text{Ph}_2\text{S}$  (Table III).

The sulfone yields are dependent on the sulfoxide concentration, the yields of  $\text{Ph}_2\text{SO}_2$  being 22, 28, 36, and 40% for the reaction with  $[\text{Ph}_2\text{SO}] = 0.01, 0.02, 0.05, \text{ and } 0.1 \text{ M}$ , respectively. A plot of  $1/[\text{sulfone yield}]$  vs.  $1/[\text{Ph}_2\text{SO}]$  is linear and the intercept is 43% yield. This probably indicates 43% selectivity for the carbonyl oxide formation according to eq 2b.

**Relative Reactivity.** As shown above, the yields of oxidation products change with the types of substrates. Competitive experiments resulted in an interesting feature of relative reactivity (Table IVA). The reactivity order with carbonyl oxide is  $\text{Ph}_2\text{SO} \gg \text{Ph}_2\text{S} > \text{C}=\text{C}$  benzene, where C=C means  $\alpha$ -methylstyrene. Sulfoxides exhibit a high reactivity and benzene is also oxidized. The resulting order is quite different from the order of  $\text{Ph}_2\text{S} \gg \text{Ph}_2\text{SO} > \text{C}=\text{C}$  with peroxy acid, a typical electrophilic oxidant (Table IVA), and also from the order of  $\text{C}=\text{C} \gg \text{Ph}_2\text{SO}, \text{Ph}_2\text{S}$  with acylperoxy radical, a radical O-transfer reagent.

The relative rates of the benzene ring hydroxylation with **7** from competitive experiments are in the order of benzene > toluene > anisole.<sup>25</sup> Although the yields are too low to obtain accurate relative rates, it is apparent that the electron-donating substituents lower the reactivity. This order is in sharp contrast to many cases of electrophilic ring hydroxylation by molecular peroxy acid,<sup>26</sup> hydroxy radical,<sup>27</sup> or phosphoranylperoxy radical.<sup>28</sup>

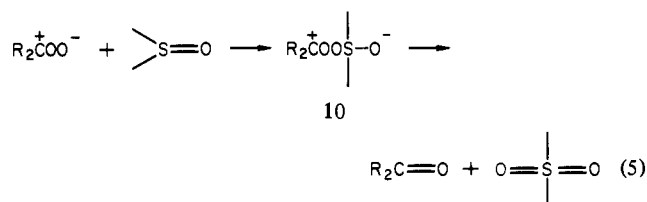
**Nucleophilic O Transfer.** Sulfoxides are known to be oxidized both electrophilically by peracids and nucleophilically by peracid anions.<sup>29</sup> The oxidation of sulfoxides is also possible by hydroperoxide anions in aprotic solvents.<sup>30</sup> Hence, the highest reactivity

Table IV. Relative Reactivities of Substrates for the O Transfers with Various Types of Peroxides

substrate	relative reactivity with		
	$\text{R}_2\text{COO}^a$	$\text{RC}(=\text{O})\text{OOH}^b$	$\text{RC}(=\text{O})\text{OO}^c$
A. Miscellaneous			
$\text{PhMeC}=\text{CH}_2$	$\sim 0.01^d$	0.045	(1.00)
$\text{Ph}_2\text{S}$	0.06	86	<0.1
$\text{Me}_2\text{SO}$	0.36	8.1	<0.1
$\text{Ph}_2\text{SO}$	(1.00)	(1.00)	<0.1
$\text{PhH}$	$\sim 0.001$	$<10^{-5}$	$<10^{-3}$
B. Substituted Diphenyl Sulfoxides <sup>e</sup>			
$(p\text{-MeOPh})_2\text{SO}$	0.72	3.64	
$(p\text{-MePh})_2\text{SO}$	0.85	2.06	
$\text{Ph}_2\text{SO}$	(1.00)	(1.00)	
$(p\text{-ClPh})_2\text{SO}$	1.33	0.307	
$\rho$ (vs. $\sigma$ )	+0.26	-1.06	
$r$	0.997	0.999	

<sup>a</sup> Relative reactivity toward carbonyl oxide **7** by competitive reactions with  $[\text{substrate}] = 0.05\text{--}0.2 \text{ M}$ ,  $[\text{7}] = 1\text{--}2 \text{ mM}$ , and  $[\text{TPP}] = 0.05 \text{ mM}$  in aerated benzene at 20 °C; irradiated at >400 nm for 30 min and determined by GLC. <sup>b</sup> By rate measurement with perbenzoic acid in benzene at 25 °C as determined iodometrically. The second-order rate constant for  $\text{Ph}_2\text{SO}$  is  $0.152 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>c</sup> By competitive reactions from ref 14. <sup>d</sup> An approximate value from the epoxide yield, but major reactions are the C-C cleavage and H-atom abstraction (see entry 7, Table III). <sup>e</sup>  $\text{Ph} = \text{C}_6\text{H}_5$  or  $\text{C}_6\text{H}_4$  and  $r$  is the correlation coefficient of the Hammett plot.

of sulfoxides toward carbonyl oxide suggests a nucleophilic oxygen atom transfer. In fact, the substituent effect on diphenyl sulfoxides gave the positive  $\rho$  value of +0.26, which is in sharp contrast with  $\rho = -1.06$  for peroxybenzoic acid in the same solvent (Table IVB). Apparently, the positive  $\rho$  value indicates a nucleophilic O transfer to sulfoxides according to eq 5. A similar mechanism is known



for the reactions of peracid<sup>29</sup> and hydroperoxide anions.<sup>30</sup> The relative reactivity and  $\rho$  value clearly suggest that the most characteristic reaction of carbonyl oxides is the nucleophilic O transfer rather than electrophilic or radical reactions.

As already mentioned, the dipolar structure **1a** is consistent with the MINDO/3 calculation, trappings by aldehydes<sup>6</sup> and MeOH, and also the facile nucleophilic oxidation of sulfoxides. However, other attempted nucleophilic reactions failed, including the Baeyer-Villiger reaction of cyclohexanone ( $\sim 1 \text{ M}$ ),<sup>31</sup> the conversion of acetonitrile or benzonitrile ( $\sim 1 \text{ M}$ ) to amides,<sup>32</sup> or the epoxidation of benzalacetone ( $\sim 0.5 \text{ M}$ ).<sup>33</sup> The failures might be due to the too short lifetime of carbonyl oxides. Recently, the Bayer-Villiger reaction of adamantanone has been proposed to go by way of a carbonyl oxide intermediate in the decomposition of furan endoperoxides.<sup>11</sup> The present result, however, seems to make the assumption less probable and some other species might participate.

(25) The relative rate ratio for the ring hydroxylation is approximately 1:0.3 for benzene-toluene.

(26) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", Elsevier Publisher, Amsterdam, 1965, p 110.

(27) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. B*, 742 (1966); *J. Phys. Chem.*, **70**, 2660 (1966).

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(31) The BV reaction of cyclohexanone is very facile: M. F. Hawthorne and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 6398 (1958).

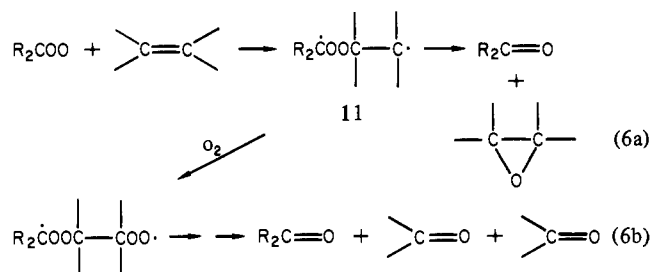
(32) The conversion of nitriles to amides is facile with alkaline  $\text{H}_2\text{O}_2$ , i.e.,  $\text{HO}_2^-$ ; L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", John Wiley and Sons, New York, 1967, p 469.

(33)  $\alpha,\beta$ -Unsaturated ketones may be epoxidized by alkaline  $\text{H}_2\text{O}_2$  and phase-transfer catalyst; R. Helder, J. C. Hummelen, R. W. P. M. Laane, J. S. Wiering, and H. Wynberg, *Tetrahedron Lett.*, 1831 (1976).

**Electrophilic O Transfer.** It is true that the oxidation of sulfides to sulfoxides proceeds via an electrophilic O transfer from carbonyl oxides since the relative reactivity of  $\text{Ph}_2\text{SO}:(p\text{-ClC}_6\text{H}_4)_2\text{SO}$  is 1:0.42.<sup>34</sup> But this electrophilic O transfer to sulfides is quite inefficient in view of the fact that sulfides are very susceptible to electrophilic oxidants such as peracid (see Table IV). O transfer to olefin is also inefficient, and the major reactions are the C–C cleavage or the allylic H-atom abstraction.

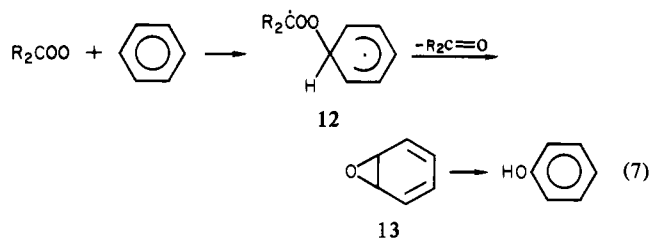
The MINDO/3 calculation on  $\text{H}_2\text{C}-\text{O}_\alpha-\text{O}_\beta$  shows a low energy level of LUMO (Table II), which suggests a high electrophilic reactivity. But the coefficients of LUMO are in the order of  $\text{C} > \text{O}_\alpha > \text{O}_\beta$ , indicating a rather lower coefficient on the actual reacting site  $\text{O}_\beta$ ; thus, carbonyl oxide is less efficient as an electrophile. It appears that the high electron affinity of the LUMO may be based on the positive charge on C and  $\text{O}_\alpha$ .

**Radical Reactions.** Radical reactions are a secondary characteristic of carbonyl oxide; it abstracts a hydrogen atom from toluene, cumene, anisole, and cyclohexane, affording the autoxidation products from these substrates. The epoxidation of aliphatic olefins is inefficient, but the allylic hydrogen abstraction is predominant. *cis*-2-Octene afforded a low-yield (only 2%) mixture of *cis* and *trans* epoxides. The mixture formation probably suggests a radical mechanism for the epoxidation (eq 6) since it is well-known that radical epoxidations afford a mixture of *cis* and *trans* epoxides.<sup>14,35</sup>



The epoxidation of styrenes is also inefficient and the ratio of epoxidation to C–C cleavage is probably determined by the reactivity of radical adduct **11**. That is, the cyclization of **11** to epoxide (eq 6a) is relatively slower than the addition of  $\text{O}_2$  to **11** leading to the C–C cleavage (eq 6b). Similar situations are known for the autoxidation of olefins.<sup>35</sup> In the case of the acylperoxy radical  $\text{RCO}_3\cdot$ , the addition and cyclization to epoxide (like eq 6a) are fast and nearly quantitative.<sup>14</sup> Therefore, it is apparent that carbonyl oxide is not efficient as a radical O-transfer agent to olefins.

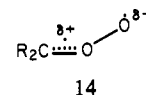
NIH shifts have been found in the hydroxylation of the aromatic ring with carbonyl oxides<sup>10b</sup> and then the hydroxylation seems to proceed via an arene oxide (**13**) as shown below in eq 7. Here,



carbonyl oxide probably adds to the aromatic ring as a radical on the basis of the following: (i) The hydroxylation of benzene is negligible with perbenzoic acid which is a potent electrophilic oxidant. (ii) No hydroxylation of benzene is known by hydroperoxide anion  $\text{ROO}^-$ . (iii) A similar radical hydroxylation is known in the autoxidation of phosphite.<sup>28</sup> (iv) The reactivity for

the hydroxylation with carbonyl oxides is in the order of benzene > toluene > anisole. These facts lead to the initial attack of the carbonyl oxide to the aromatic ring as an anionic radical to yield the adduct **12**, which may cyclize to arene oxide **13** like the olefin epoxidation (eq 6a). The relative reactivity of substituted benzenes (item iv) is quite different from other electrophilic hydroxylations with  $\text{HO}\cdot$ <sup>27</sup> or peracids<sup>26</sup> but is consistent with the nucleophilic nature as an anionic radical.

This reactivity as a radical may be understood on the basis of diradical structure **1c**. Although the MINDO/3 analysis suggests the dipolar structure **1a**, many rigorous calculations<sup>15</sup> always indicated the biradical one **1c**. But it is not easy to comprehend why radical **1c** resists against the oxygen addition to the radical site on carbon in spite of the fact that the usual carbon radicals are trapped by oxygen in a diffusion-controlled rate. It seems then to be more appropriate to assume carbonyl oxide is a resonance hybrid between **1a** and **1c**, that is, **14**. The dipolar biradical



**14** seems to characterize all the reactivities of carbonyl oxide in solutions, e.g., the nucleophilic O transfer, trapping by methanol, radical additions to olefins or aromatic rings, hydrogen atom abstraction as a radical, and a rather poor reactivity as an electrophilic oxidant. Carbonyl oxides may be understood to exhibit variable features of reactions according to the substrates attacked.

### Experimental Section

Melting points are corrected. <sup>1</sup>H NMR spectra were recorded with a Hitachi R24B spectrometer. GLC analyses were performed with a Yanagimoto G180 gas chromatograph, using two different columns; PEG 20M, 10% on Chromosorb W; Silicone OV-17, 5% on Shimalite W. GC-MS analysis was carried out with a Shimadzu GCMS 7000 spectrometer.

**Materials.** 9-Diazo fluorene (**6**) was prepared from the hydrazone<sup>36</sup> and recrystallized from hexane–ether, mp 98–99 °C (lit.<sup>36</sup> mp 99 °C). Diphenyldiazomethane (**5**) was synthesized similarly and extracted with hexane before use. Substituted diphenyl sulfoxides were prepared from corresponding benzenes and thionyl chloride<sup>37</sup> in 40–50% yields and recrystallized from benzene–hexane; *p,p'*-dimethyl, mp 95–97 °C (lit.<sup>38</sup> mp 92 °C); *p,p'*-dichloro, mp 143–145 °C (lit.<sup>37</sup> mp 143–144 °C); *p,p'*-dimethoxy, mp 100–101 °C (lit.<sup>39</sup> mp 96 °C). Authentic 2-phenylallyl alcohol (**9**) and 2-phenylacrolein (**8**) were prepared by the  $\text{SeO}_2$  oxidation of  $\alpha$ -methylstyrene.<sup>40</sup>

**Typical Procedure of the Photooxidation.** A 3-mL aerated benzene solution of 0.2 M  $\alpha$ -methylstyrene, 1 mM diazo fluorene (**6**), and 0.05 mM *meso*-tetraphenylporphine (TPP) in a 10 mL test tube was irradiated with a 300-W medium-pressure Hg lamp through a 5%  $\text{NaNO}_2$  filter solution (i.e., >400 nm) for 30 min at 20 °C. The conversion to **6** was usually complete in 10 min. Products were determined by GLC and identified by GC-MS analysis in comparison to authentic samples. The result for  $\alpha$ -methylstyrene is listed as entry no. 7 in Table III; the GLC analysis indicated other unidentified product in a few percent yield. The acrolein **8** was also identified by the  $\text{NaBH}_4$  reduction to allyl alcohol **9**.

**Photooxidation of Diphenyldiazomethane (5) in the Presence of MeOH.** A solution of 50 mg of **5** and 4 mg of Rose Bengal in  $\text{CH}_2\text{Cl}_2$  (15 mL)–MeOH (5 mL) was irradiated through a Pyrex filter at 0 °C with oxygen bubbling for 10 min. The reaction mixture was washed with water and dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated at slightly reduced pressure. The NMR spectra of the crude product mixture indicated the formation of 29% yield of  $\alpha$ -hydroperoxy- $\alpha$ -methoxydiphenylmethane (**4**, R = Ph) in addition to 10%  $\text{Ph}_2\text{C}=\text{O}$  and 60%  $\text{Ph}_2\text{C}=\text{O}$ . The hydroperoxide could be purified by the extraction with 0.1% NaOH aqueous solution; the neutralization with AcOH and the extraction with  $\text{CH}_2\text{Cl}_2$  gave a pure sample, mp 62–63 °C (lit.<sup>41</sup> mp 62–64 °C). The NMR spectra of the purified  $\text{Ph}_2\text{C}(\text{OMe})\text{OOH}$  exhibited a singlet at  $\delta$  3.25 (3 H) as did the authentic sample.<sup>41</sup> By the

(34) Recently, an electrophilic oxidation of diphenyl sulfides has been reported, i.e.,  $\rho = -0.32$  with  $^1\text{O}_2$  and  $\alpha$ -benzoylphenyldiazomethane. W. Ando, Y. Kabe, and H. Miyazaki, *Photochem. Photobiol.*, **31**, 191 (1980).

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way, benzhydryl methyl ether possesses singlet peaks at  $\delta$  3.29 (3 H) and 5.11 (1 H).

**Photooxidation of 9-Diazofluorene (6) in the Presence of MeOH.** A similar procedure showed the formation of a 34% yield of 9-hydroperoxy-9-methoxyfluorene (**4**,  $R_2 = 9$ -fluorenyl) in addition to 9-methoxyfluorene (3%) and fluorenone (63%).

The purification by the extraction with 0.1% NaOH, neutralization with AcOH, and extraction with  $\text{CH}_2\text{Cl}_2$  gave pure (by NMR) 9-hydroperoxy-9-methoxyfluorene; we could not crystallize it. Its NMR spectra ( $\text{CCl}_4$ )  $\delta$  3.35 (singlet, 3 H) 7.3-7.8 (multiplet, 8 H), and 8.7

(broad s, 1 H) are different from those of 9-methoxyfluorene with  $\delta$  3.05 (s, 3 H) and 5.59 (s, 1 H),<sup>42</sup> supporting the  $\alpha$ -methoxy hydroperoxide structure. The hydroperoxide is reduced by KI to fluorenone at 50 °C in AcOH-MeOH-H<sub>2</sub>O (1:1:2).

**Acknowledgment.** We are grateful to Dr. Kimihiko Hirao for his aid in the calculation of MINDO/3 and to Dr. Kohtar Tomizawa for his aid in the measurement of GC-MS spectra. The MO calculations were carried out on a FACOM-M200 of the Nagoya University Computational Center.

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## Monoradical Rearrangements of the 1,4-Biradicals Involved in Norrish Type II Photoreactions

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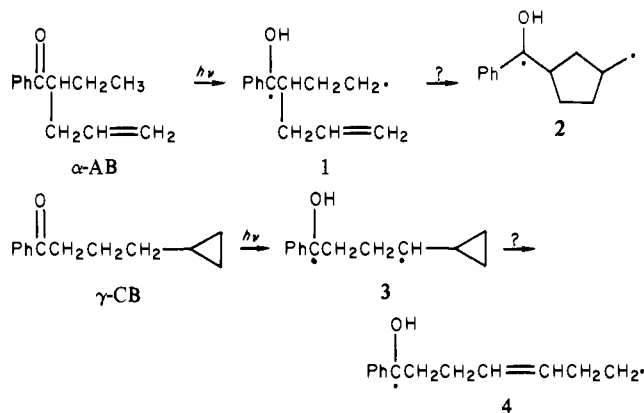
**Abstract:** The photochemistry of  $\alpha$ -allylbutyrophenone ( $\alpha$ -AB) and that of  $\gamma$ -cyclopropylbutyrophenone ( $\gamma$ -CB) both reveal that the 1,4-biradicals generated by triplet-state  $\gamma$ -hydrogen abstraction undergo typical radical rearrangements in competition with their more normal type II reactions. From  $\alpha$ -AB, 2-phenyl-2-norbornanol is formed in  $1/24$ th the combined yield of 1-phenyl-4-penten-1-one and 1-phenyl-2-allylcyclobutanol. Its formation is explained by a 5-hexenyl-to-cyclopentylmethyl rearrangement of the 1,4-biradical, with a rate constant of  $5 \times 10^5 \text{ s}^{-1}$ . From  $\gamma$ -CB, 1-phenyl-4-hepten-1-one and 1-phenyl-4-cycloheptenol together are formed in double the yield of acetophenone. Their formation is explained by a cyclopropylcarbinyl-to-allylcarbinyl rearrangement of the 1,4-biradical, with a rate constant of  $2 \times 10^7 \text{ s}^{-1}$ . In both cases, the rearrangement percentages are what would be predicted if the biradicals have the same 35-50-ns lifetime measured for other ketones and if they rearrange with the same rate constants characteristic of monoradicals. Triplet  $\gamma$ -CB decays only 1.5 times faster than triplet  $\gamma$ -isopropylbutyrophenone, indicating that there is at most a small enhancement of the  $\gamma$ -hydrogen abstraction rate by cyclopropyl conjugation. Triplet  $\alpha$ -AB decays 100 times faster than triplet butyrophenone, 99% representing internal quenching by the  $\beta$ -vinyl group ( $k = 8 \times 10^8 \text{ s}^{-1}$ ). Bicyclic oxetanes are formed in quantum yields of only 0.01. No oxetanes were isolated, only rearranged unsaturated alcohols and aldehydes.

### Introduction

Since we first successfully trapped the 1,4-biradicals known to be involved in Norrish type II photoelimination and cyclization,<sup>2</sup> there has been considerable interest in the factors which influence the behavior of such intermediates.<sup>3</sup> The fact that the first trapping reaction involved hydrogen atom abstraction from a thiol prompted two related questions: (1) Do monoradical reactions of biradicals occur with the same rate constants as those of simple radicals? (2) If so, can competitive monoradical reactions be used to determine biradical lifetimes?

In the expectation that the answer to the first question is "yes", we prepared two ketones which, upon triplet state  $\gamma$ -hydrogen abstraction, would form biradicals which could undergo characteristic free-radical rearrangements. We have already communicated a positive result for  $\alpha$ -allylbutyrophenone ( $\alpha$ -AB).<sup>4</sup> This paper reports our complete results for both ketones.

About the time we finished these experiments, Scaiano reported the first direct flash spectroscopic determination of type II biradical lifetimes.<sup>5</sup> This independent experimental capability minimizes



the importance of the second question presented above but allowed us to focus on the more fundamental first question. Coupled with Beckwith's recent extensive study of structural effects on free-radical rearrangement rates,<sup>6</sup> our results allow the conclusion that

(1) Visiting scholar on funds provided by the Fuji Photo Film Co. Ltd., Tokyo, Japan.

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