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Mechanism of Ester Formation in the Photosensitized Oxidation of Diazomethanes. Carbonyl Oxides Do Not Isomerize to Dioxiranes in Solution

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Formation of esters in the photooxidation of diazomethanes has been studied mechanistically. Unimolecular rearrangement of carbonyl oxides via dioxiranes as often proposed was ruled out clearly by ^{18}O-tracer experiments. For the case of alkylphenyldiazomethanes, the rearranged alkyl benzoates were shown to be formed by a radical chain decomposition involving alkoxyl radicals as a chain carrier. The mechanism was confirmed chiefly by the ^{18}O-tracer study and crossover experiments in the formation of esters. Other cases as reported to involve a rearrangement of carbonyl oxides to form esters or anhydrides were demonstrated to be the result of the Baeyer–Villiger oxidation by the oxide intermediates. The barrier preventing the isomerization of carbonyl oxides to more stable dioxiranes is discussed.

Carbonyl oxides **1** are important intermediates in the ozonolyses of olefins[1] and have attracted much attention as a model for monooxygenase enzymes.[2] The oxides can also be generated by the reaction of triplet carbenes with oxygen[3] or the singlet oxygen oxidation of diazoalkanes[4] and have recently been observed directly on the laser flash photolysis in solution[5] and by IR spectroscopy in low temperature matrices.[6] The intermediacy of **1** has been suggested in the decomposition of furan endoperoxides[7] and in the reaction of singlet oxygen with ylides,[8] azines,[9] and methylenecyclopropanes.[10]

Carbonyl oxides may transfer an oxygen atom to alkanes,[11] alkenes,[12] aromatic rings,[13] and sulfides,[14] and the most characteristic reaction is a nucleophilic O-transfer as shown in the oxidation of sulfoxides[15] and electron-deficient olefins.[16] Recently, the cycloaddition of **1** not only with aldehydes[17] but with ketones,[18] esters,[19] and alkenes[20] has been demonstrated.

The structures and stabilities of carbonyl oxides **1** and their isomers, dioxirane **2** and dioxymethane biradical **3**, have been of theoretical interest,[21,22] dioxirane **2** being

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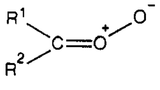
Table I. Photooxidation of Ethylphenyldiazomethane (4a)

run no.	conditns[a] sens/solvent/time	product yields (%)[b] PhCOEt	PhCO$_2$Et	PhCH=CHMe	others
1	TPP/PhH/30 min	90	6.9	0.5	PhOH (1)
2	TPP/PhH/Me$_2$SO (1 M)/5 min	96	2.6	0.5	PhOH (0.2); Me$_2$SO$_2$ (43)
3	None/PhH/6 h[c]	41	3.3	46 (3)[d]	PhOH (1)
4	TPP/PhH-MeOH/30 min	54	0.8	0.5	PhCO$_2$Me (41)
5	RB/MeOH/15 min (0 °C)	35	0.4	5	Ph(Et)C(OMe)OOH (30); PhCO$_2$Me (4)

[a] Irradiation of 0.01 M **4a** and 0.1 mM TPP at >400 nm under oxygen at ca. 20 °C if not noted otherwise. RB is Rose Bengal. [b] Product yields were determined by GLC or NMR and based on **4a**. [c] Direct irradiation at >400 nm. [d] Value in parentheses is a ratio of trans/cis.

calculated to be 30–40 kcal/mol more stable than 1. It is interesting to ascertain whether or not 1 could isomerize to 2. Theoretical calculations have indicated a relatively high activation energy (i.e., 20–30 kcal/mol) for the isomerization.[22]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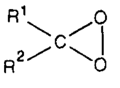
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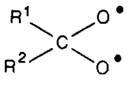
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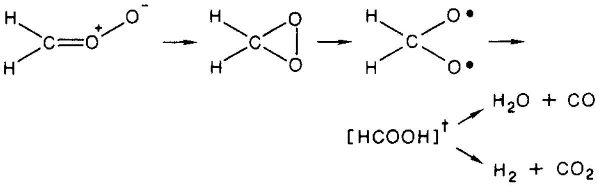
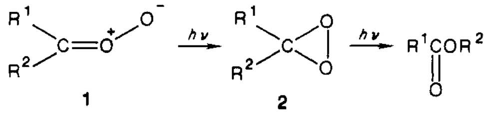
In the gas phase a reaction scheme involving an excited formic acid has been proposed on the basis of decomposition products in the ozonolysis of ethylene[23] and from the observation of vibrationally excited carbon monoxide in the reaction of methylene with O$_2$.[24] More directly, a



(1)

parent dioxirane (2, R^1 = R^2 = H) was identified in the gas phase by microwave and mass spectroscopies at low temperature.[25] On the other hand, carbonyl oxides, formed by the addition of O$_2$ to carbenes in low temperature matrices, have been shown to give rearranged esters presumably via dioxiranes.[6,26] Recent detailed studies in low temperature matrices have demonstrated that the irradiation of 1 affords dioxirane 2 and its further irradiation leads to rearranged esters as shown in eq 2.[6d]



1 2 (2)

As mentioned above, the formation of 2 from 1 has been clarified in the gas phase and in low temperature matrices but never been proved clearly in solution in spite of repeated suggestions for such a rearrangement.[7,9,10,27-29] An alternative method to generate 2 in solutions has been developed by the caroate oxidation of ketones.[30] Dimethyldioxirane (2, R^1 = R^2 = Me) is shown to be metastable in acetone and identified by various spectroscopies.[30i,l-n] It is interesting to note that the dioxirane shows an electrophilic oxenoid character in sharp contrast to the nucleophilic nature of carbonyl oxides.[12e,15]

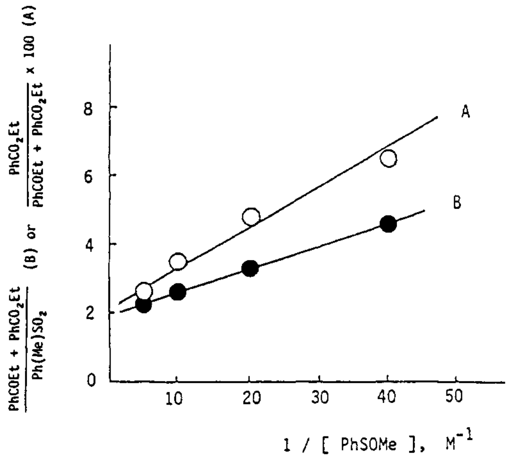


Figure 1. Reciprocal plots for the effect of phenyl methyl sulfoxide (0.025–0.2 M) on the ester (A) and sulfone yields (B) in the photooxidation of ethylphenyldiazomethane **4a**. **4a** (6.4 mM) and TPP (0.2 mM) were irradiated at >400 nm in MeCN–PhH (4:1) under oxygen.

The formation of rearranged products in ozonolyses has been known for a long time as so-called "abnormal

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Table II. Photooxidation of Substituted Phenyldiazomethanes Ph(R)CN_2

		product yields (%)[b]			$\frac{PhCO_2R}{PhCOR} \times 100$
diazomethane	conditns[a]	PhCOR	$PhCO_2R$	PhCH=CHR′[c]	
4a, R = Et	TPP/PhH	90	6.9	0.5	7.7
4b, R = Me	TPP/PhH	84	5.7	0.4	6.8
4c, R = CH_2Ph	TPP/PhH	34	3.1	44 (9.1)	9.1
4d, R = CH(Me)Ph	TPP/C_6H_{12}	65	7.0	13 (1.7)	10.7
4e, R = H	TPP/C_6H_{12}	84	(3)[d]		(<3)[d]
4f, R = Ph	TPP/C_6H_{12}	95	0		0

[a] Irradiated at >400 nm under oxygen for 10–60 min (~0.01 M 4 and 0.1 mM TPP); C_6H_{12} = cyclohexane. [b] See footnote b in Table I. [c] Olefins by 1,2-hydrogen shift of carbenes. The values in parentheses are the ratios of trans/cis. [d] Benzoic acid may also be produced by the autoxidation of PhCHO formed.

ozonolyses".[31] Various schemes have been proposed to account for the rearrangements as summarized in the following: (i) an intramolecular rearrangement of 1 via 2;[27,28] (ii) a Baeyer–Villiger-type oxidation of ketones by 1;[32] (iii) a rearrangement upon decomposition of unstable secondary ozonides;[33] and as for the formation of rearranged anhydrides in ozonation of acetylenes and α,β-unsaturated ketones, (iv) a decomposition of trioxabicyclo[2.1.0]pentanes formed by an intramolecular cycloaddition of 1 to adjacent carbonyl group.[28,34] Although the pathways ii–iv may be partly verified by control experiments, acceptable reaction schemes in the ozonolysis cannot be concluded unless the unimolecular pathway i is shown not to be occurring.

Rearranged products are also reported in the $^1O_2$ oxidation of diazoalkanes,[29] azines,[9] and methylenecyclopropanes[10] and on the decomposition of furan endoperoxides.[7c–f] Though most of these authors prefer the pathway i, no definitive mechanisms have been established. We have noted previously that rearranged alkyl benzoates are formed in the photooxidation of alkylphenyldiazomethanes[35] and reported a preliminary result against the unimolecular pathway i.[36] We report here that the esters are formed by a radical chain decomposition of alkylphenyldiazomethanes involving alkoxyl radicals and that the unimolecular rearrangement of carbonyl oxides does not occur for all cases examined, eliminating pathway i, which is often suggested in the literature.

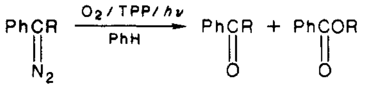
Results and Discussion

Formation of Esters on the Photosensitized Oxidation of Alkylphenyldiazomethanes 4. Irradiation of 0.01 M ethylphenyldiazomethane (**4a**) and 0.01 mM *meso*-tetraphenylporphine (TPP) in benzene at >400 nm under oxygen afforded propiophenone (90%) and ethyl benzoate (7%) together with a small amount of phenol (run 1 in Table I). The yields of the ester decreased significantly by adding methyl phenyl sulfoxide (run 2 in Table I and Figure 1), suggesting that the carbonyl oxide intermediate might participate in the ester formation since sulfoxides are known to trap carbonyl oxide 1 efficiently.[15a] The addition of methanol also suppressed the yields of ethyl benzoate and afforded Ph(Et)C(OMe)OOH as a adduct of 1 with methanol, the prolonged irradiation of which led to methyl benzoate as a major product of radical decomposition.[15a]

Table III. Mass Spectral Data for the ^{18}O-Tracer Study in the Photooxidation of Ph(R)C=N_2[a]

	$PhCO_2R$		
diazomethane	M	M + 2	M + 4
	Observed		
4e (R = H)	100	52.7 ± 0.8	7.8 ± 0.2
4b (R = Me)	100	48.0 ± 0.8	6.1 ± 0.3
4a (R = Et)	100	55.5 ± 1.8	9.1 ± 0.5
4a (R = Et)[b]	100	52.8 ± 1.6	7.4 ± 0.5
	Calculated		
retention	100	1.2	27.9
scramble	100	56.4	7.9

[a] Starting oxygen gas; $^{16}O{-}^{16}O$:$^{16}O{-}^{18}O$:$^{18}O{-}^{18}O$ = 100:(1.17 ± 0.02):(27.9 ± 0.1). See Experimental Section for details. [b] The autoxidation of the diazo compound at room temperature in the dark for 3 days.



$$\underset{\mathbf{4}}{\underset{N_2}{\overset{\|}{PhCR}}} \xrightarrow[PhH]{O_2/TPP/h\nu} \underset{\mathbf{5}}{\underset{O}{\overset{\|}{PhCR}}} + \underset{\mathbf{6}}{\underset{O}{\overset{\|}{PhCOR}}} \qquad (3)$$

The TPP-sensitized photooxidation of other phenyldiazomethanes (4, R = alkyl) proceeded in a similar manner to the case of **4a** (Table II). Interestingly, the resulting ratios of $PhCO_2R$/PhCOR were rather constant in the range of 0.07–0.10 for 4 with R = Me, Et, CH_2Ph, and CH(Me)Ph. A small amount of benzoic acid was obtained in the photooxidation of **4e** (R = H). But, it is not certain whether the acid was formed via the same pathway as **4a–d** or by the autoxidation of PhCHO produced. It is notable that phenyl esters were not detected from the reaction of **4a–d** and that diphenyldiazomethane (**4f**) afforded no ester. The resulting aptitude of rearrangement, Me ~ Et ~ CH_2Ph ≫ Ph, might reflect the relative stabilities of departing radicals from alkoxyl radicals as observed in the homolytic rearrangement of diradicals from β-peroxyesters.[37]

The mechanism for the ester formation is interesting because the reaction pathway 1 → 2 → ester (cf. eq 1 or 2) may involve the rearrangement of carbonyl oxides and dioxiranes. To test the possibility of such rearrangements in solution is also pertinent from the standpoint of theoretical expectations.[21,22] Therefore, we studied in detail the mechanism for the ester formation from diazo compounds.

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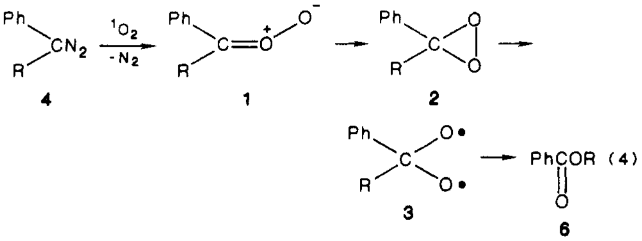
Table IV. Mass Spectral Data for the ^{18}O-Tracer Study in the Photooxidation of $Ph(Me_3Si)C{=}N_2$ (4g)

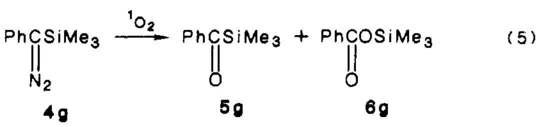
starting oxygen gas	PhCO$_2$SiMe$_3$ (6g)				
	M	M + 1	M + 2	M + 3	M + 4
			Observed		
$^{16}O_2$	100	99.6 ± 1.6	24.1 ± 0.2	9.1 ± 0.5	1.2 ± 0.1
$^{16}O_2$–$^{18}O_2$[a]	100	90.3 ± 0.7	35.3 ± 2.3	20.3 ± 1.0	4.4 ± 0.3
			Calculated[b]		
retention	100	99.6	24.7	9.7	9.8
scramble	100	99.6	40.9	25.8	5.9

[a] Starting gas; ^{16}O–^{16}O:^{16}O–^{18}O:^{18}O–^{18}O = 100:(0.62 ± 0.04):(8.35 ± 0.22). See Experimental Section for details. [b] Calculated values from the observed data of an authentic sample of **6g** and the above content of $^{16}O_2$–$^{18}O_2$. The mass spectrum of **6g** was somewhat complex because of significantly enhanced M + 1 peak and M + 2 peak of Si.

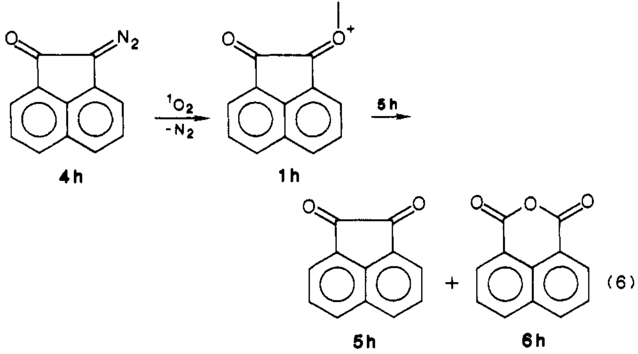
Plausible Mechanisms for Ester Formation. (A) Unimolecular Rearrangement of Carbonyl Oxides. The migratory aptitude alkyl ≫ aryl, observed for the ester formation, seems to be consistent with a scheme involving a rearrangement of R$^\bullet$ via dioxymethane biradical 3 (eq 4). If the unimolecular reaction is operative, the two oxygen atoms in the ester should be originated from the same oxygen molecule. In order to ascertain the scheme, we undertook a tracer study using a mixture of $^{16}O_2$–$^{18}O_2$. According to the unimolecular rearrangement of 1, doubly labeled $^{18}O_2$ should be retained in the ester without any scrambling. To our surprise, the data in Table III indicate complete scrambling of the two oxygens, exhibiting that each oxygen on the ester comes from different O_2 molecules. Thus the unimolecular pathway (eq 4) is clearly ruled out.



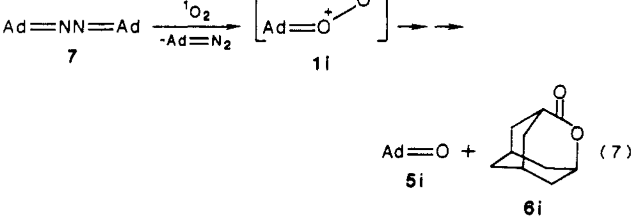
Then we undertook similar ^{18}O-tracer experiments on reported cases of rearrangements in the oxidation of diazo compounds. Ando et al. reported a formation of trimethylsilyl benzoate (**6g**) from (trimethylsilyl)phenyldiazomethane (**4g**)[29b,d] (eq 5). Silyl carbonyl oxide (1, R = SiMe$_3$) was expected to rearrange to dioxirane 2 intramolecularly because of the high affinity of silicon atom toward oxygen atom. The ^{18}O-tracer experiment, however, resulted in the complete scrambling of oxygens as shown in Table IV, eliminating clearly the unimolecular pathway. The reported formation of 1,8-naphthalic anhydride (**6h**) on the photooxidation of 7-diazo-8-acenaphthenone (**4h**)[29c] (eq 6) was likewise shown not to proceed unimolecularly by the ^{18}O-tracer experiment in Table V. As stated in the next section, anhydride **6h** is produced via the Baeyer–Villiger oxidation of **5h** by carbonyl oxide **1h**.

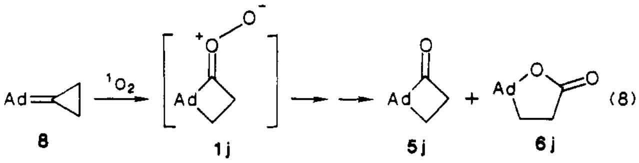


$$\underset{\mathbf{4g}}{\mathrm{PhC(=N_2)SiMe_3}} \xrightarrow{^1O_2} \underset{\mathbf{5g}}{\mathrm{PhC(=O)SiMe_3}} + \underset{\mathbf{6g}}{\mathrm{PhC(=O)OSiMe_3}} \quad (5)$$



We also examined rearrangement products from substrates other than diazo compounds. Ando et al. reported the photooxidation of adamantanone azine (**7**) to yield lactone **6i** in addition to adamantanone **5i** (eq 7).[9a,c] Since the yield of **6i** was decreased by adding methyl phenyl sulfoxide, carbonyl oxide **1i** was thought to be involved for the lactone formation. Similarly, the formation of five-membered lactone **6j** was reported in the reaction of adamantylidenecyclopropane (**8**) with singlet oxygen.[10a]





Here, the unimolecular rearrangement of carbonyl oxides via dioxirane intermediates was also suggested. However, the $^{18}O_2$-tracer study in Table V resulted in the complete scrambling of two oxygen atoms in lactones, **6i** and **6j**, eliminating the proposed unimolecular rearrangement.

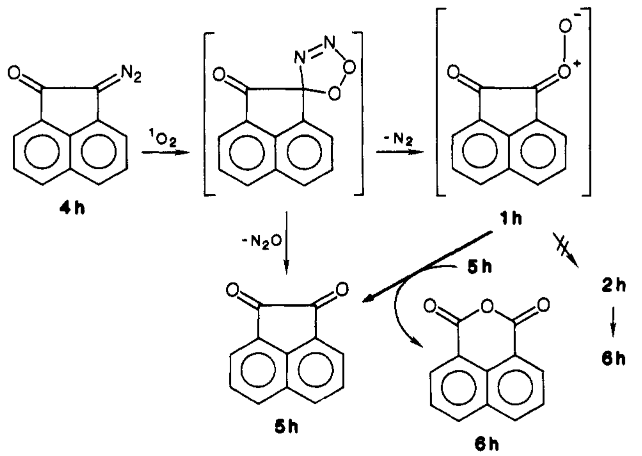
Thus, it may be concluded that a unimolecular pathway such as 1 → 2 → 3 → rearranged product is not operative in general.

Table V. Mass Spectral Data for ^{18}O-Tracer Study in the Photooxidation of 4h, 7, and 8[a]

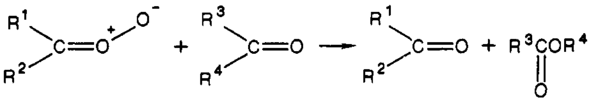
reactant	condition	convrsn (%)	product (%)[b]	mass spectral data M	M + 2	M + 4
		Observed				
4h	TPP/PhH/*hν* (0.5 h)	100	**6h** (53)	100	15.9 ± 1.1	1.0 ± 0.2
7	TPP/PhH-MeCN (1:4)/*hν* (10 h)	38	**6i** (24)	100	11.4 ± 0.3	0.5 ± 0.1
8	MB/MeCN/*hν* (0.5 h)	50	**6j** (68)	100	16.3 ± 0.6	1.0 ± 0.3
		Calculated				
	retention			100	0.6	8.4
	scramble			100	16.8	0.7

[a] Starting oxygen gas; ^{16}O–^{16}O:^{16}O–^{18}O:^{18}O–^{18}O = 100:(0.62 ± 0.04):(8.35 ± 0.22). See Experimental Section for details. [b] Selectivity % of ester or anhydride.

Scheme I



(B) Baeyer–Villiger Oxidation of Ketones. As described in earlier reports,[32] the esters might be formed by the Baeyer–Villiger oxidation of ketones with **1** (eq 9).



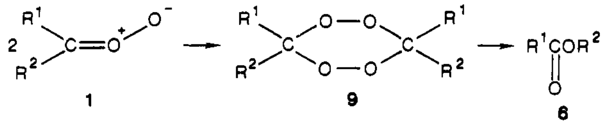
$$R^1R^2C{=}\overset{+}{O}{-}O^- + R^3R^4C{=}O \rightarrow R^1R^2C{=}O + R^3COR^4 \quad (9)$$

However, the oxidation was not operative for the present formation of alkyl benzoates from diazomethanes **4** as revealed by control experiments; the TPP-sensitized photooxidation of 0.01 M ethylphenyldiazomethane (**4a**) in the presence of 0.01 M acetophenone (**5b**) afforded no methyl benzoate (**6b**), and the yield of ethyl benzoate (**6a**) was not affected by the addition of **5b**.

As an exceptional case, acenaphthenequinone (**5h**, 8.0 mM) was converted to 1,8-naphthalic anhydride (**6h**) during the photooxidation of Ph_2CN_2 (14.5 mM) or $PhCOC(N_2)Ph$ (7.8 mM), the product ratios being **6h**/Ph_2CO = 0.31 or **6h**/PhCOCOPh = 0.19. This suggests that quinone **5h** is oxidized to anhydride **6h** by carbonyl oxides according to eq 9. So far, unimolecular rearrangement of carbonyl oxide **1h** has been suggested for the formation of **6h** because the addition of **5h** did not increase the yield of **6h**.[34c] However, the corresponding ^{18}O-tracer study on the photooxidation of **4h** (Table V) denied the unimolecular rearrangement of **1h** via **2h**. Moreover, we found that the ratio of evolved gas (N_2O/N_2 = 45/55) on the photooxidation of **4h** was comparable to the corresponding product ratio (i.e., **5h**/**6h**) of 47/53. Then, it may be concluded that carbonyl oxide **1h** generated is effectively trapped by **5h** to give **6h** as shown in Scheme I.

Adamantanone **5i** was shown to be oxidized to lactone **6i** with carbonyl oxides,[7c,33b] suggesting that the lactone formation in eq 7 proceeds via the Baeyer–Villiger oxidation of **5i** with **1i**. Likewise, ketone **5j** was evidenced to be oxidized to lactone **6j**.[10a] Thus the Baeyer–Villiger reaction operates only in the particular cases of eq 6, 7, and 8, but it cannot be accepted for more general ones of $R^1R^2C{=}N_2$.

(C) Ester Formation via Ketone Diperoxides. The formation of ketone diperoxide **9** by a dimerization of carbonyl oxides has been reported in the ozonation of olefins[1] and the oxidation of diazoalkanes.[3b] However, under the present conditions of photooxidation of **4** we could not detect **9** in the reaction mixture.

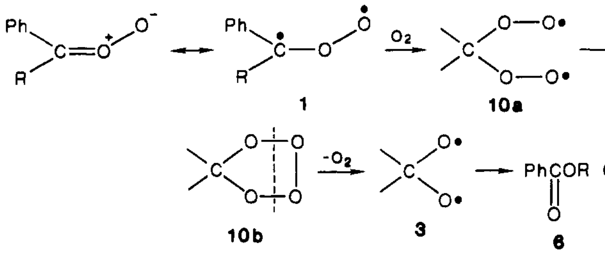


$$2\,R^1R^2C{=}\overset{+}{O}{-}O^- \rightarrow \underset{9}{R^1R^2C(OO)_2CR^1R^2} \rightarrow R^1COR^2 \quad (10)$$

1 9 6

Thermal[38] or metalloporphyrin-catalyzed[39] decomposition of **9** has been reported to give a small amount of esters. Then we examined acetophenone diperoxide (**9b**, R_1 = Ph, R_2 = Me) and confirmed that the diperoxide was stable under photooxidation conditions and unreactive toward diazo compounds. These facts indicate no participation of **9** for the formation of esters.

(D) Rearrangement via Cyclic Tetraoxide 10b and Diradical 3. As pointed out by many theoretical calculations,[21] a simple restricted-Hartree–Fock (RHF) solution cannot give a correct description of carbonyl oxide **1**, which indicates the importance of diradical character of **1**.[40] Therefore, the addition of O_2 to the radicaloid carbon of **1** may occur and generate a cyclic tetraoxide (**10b**), which eliminates O_2, as in the case with acyclic tetraoxides,[41] to afford biradical **3** and then ester (eq 11). This mechanism



1 10a 10b 3 6 (11)

is consistent with the complete scrambling of oxygen atoms in the ^{18}O-tracer study.[36] However, a tenfold decrease in oxygen pressure did not affect the ester yield, suggesting the unimportance of the addition of O_2 to **1**.[42] More conclusively, the scheme of eq 11, although attractive, was ruled out by cross experiments as described in F.

(E) Ester Formation via an Ozone–Diazoalkane Reaction. A generation of ozone by the reaction of carbonyl oxides with O_2 has been proposed on the basis of IR spectroscopy[26b,c] and chemiluminescence from carbene and oxygen.[43] Although the ozone oxidation of diazo compounds is known to give ketones,[44] there is no evidence for the formation of **1** during the oxidation. As an exceptional case, ester RCO_2SiMe_3 was formed on the ozone oxidation of $Me_3Si(R)CN_2$,[45] but the participation of carbonyl oxides was not clear since silyl ketones were facilely converted to esters by ozonation.[45]

We examined the ozone oxidation of ethylphenyldiazomethane (**4a**) in CCl_4 at 0 °C; the product was only PhCOEt (**5a**) and no ester was detected. Thus, it is apparent that ozone is not involved in the ester formation.

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(42) As an alternative pathway, 1,3-dipolar cycloaddition of **1** with $^1O_2$ may give **10b** because **1** is a 1,3-dipole with a 4π-electron system.[13] However, the ester yields were almost unchanged even when the irradiating light intensity was changed ten times, eliminating the pathway.

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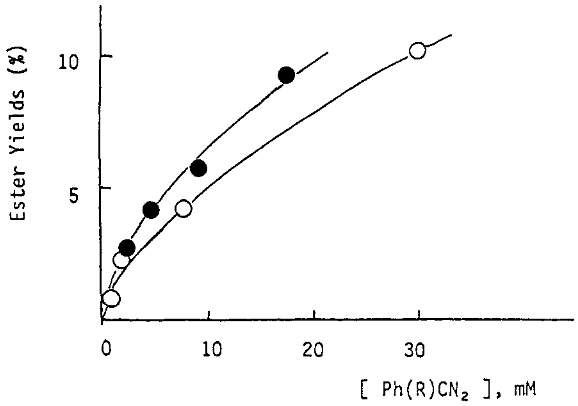
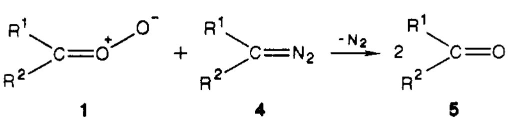


Figure 2. Effect of initial concentrations on the ester yields for the photooxidation of alkylphenyldiazomethane in the presence of 0.2 mM TPP in MeCN–PhH (4:1) under oxygen: (○) **4b** (R = Me); (●) **4a** (R = Et).

(F) Ester Formation by Radical Chain Decomposition. It is known that carbonyl oxides react with diazoalkanes to give two molecules of ketones (eq 12) as a main process for the photooxidation of diazo compounds, the bimolecular rate constant being 4×10^5 M^{-1} s^{-1} for $R^1 = R^2 = Ph$.[5b] Therefore, if esters are formed from carbonyl oxides in competition with the reaction of eq 12, the ester yields should be suppressed by increasing the concentrations of **4**. Contrary to the expectation, the ester yields were decreased with the more diluted solution of **4** as shown in Figure 2. The rearranged ester increased with increasing concentrations of **4**, suggesting a radical chain reaction for the ester formation. The necessity of diazo compounds for the ester formation was confirmed by the fact that no detectable amount of $PhCO_2Et$ (**6a**) was formed on the ozonolysis of Ph(Et)C=C(Et)Ph (**11a**). Thus esters are formed from carbonyl oxides only in the presence of diazoalkanes.

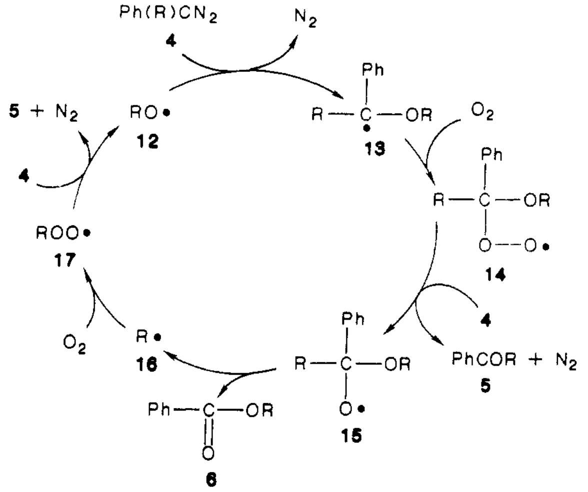

$$R^1R^2C{=}\overset{+}{O}{-}O^- \;(\mathbf{1}) + R^1R^2C{=}N_2 \;(\mathbf{4}) \xrightarrow{-N_2} 2\, R^1R^2C{=}O \;(\mathbf{5}) \quad (12)$$

To our surprise, the "rearranged" esters were found to be a cross product, i.e., the photooxidation of a 1:1 mixture of $C_6H_5(CH_3)CN_2$ (**4b**) and $C_6D_5(CD_3)CN_2$ (**4b**-d_8) gave $C_6H_5CO_2CH_3$, $C_6H_5CO_2CD_3$, $C_6D_5CO_2CH_3$, and $C_6D_5CO_2CD_3$ with a ratio of 1:1:1:1. This shows a complete scramble of alkoxyl and acyl groups in the esters obtained.

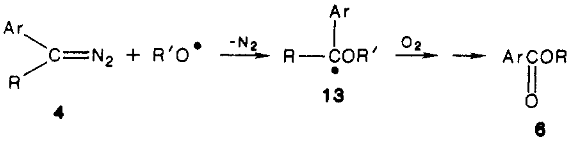
The important results described above are that (i) the esters are formed with complete scrambling of two oxygen atoms and also between alkoxyl and acyl groups and (ii) the diazo compounds are essential for the ester formation. These facts led us to an unexpected mechanism for the ester formation, i.e., a radical chain decomposition of alkylphenyldiazomethane **4** involving alkoxyl radical RO• (**12**) as a chain carrier (Scheme II). To confirm the chain mechanism, we carried out two experiments as follows:

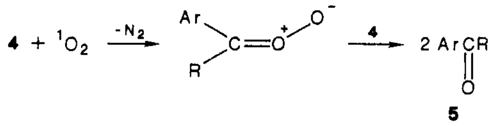
(i) Alkoxyl radicals RO• generated from other sources may initiate the chain reaction. We used as a RO• source di-*tert*-butyl peroxyoxalate (**18**), which was reported to decompose to *t*-BuO• and CO_2 with the rate constant of 10^{-3} s^{-1} at 55 °C in benzene.[46a] The autoxidation (55 °C, 1 h) of Ph(Me)CN_2 (**4b**, 13.4 mM) in the presence of **18** (0.75 mM) in aerated benzene afforded a mixture of PhCOMe (64.9%), $PhCO_2Me$ (16.4%), and $PhCO_2$-*t*-Bu (4.7%). It is apparent that *t*-BuO• generated from **18** attacks **4b** to produce $PhCO_2$-*t*-Bu and initiates the chain decomposition of **4b** to yield the ketone and esters. The addition of cumene (1 M) exhibited practically no effect on the product ratio in the thermolysis of **4b** and **18**. In other words, the presence of **4b** suppressed the autoxidation of cumene initiated by *tert*-butoxyl radical. Thus, RO• reacts selectively with diazomethane **4b** at least 10^3 times faster than the hydrogen abstraction from cumene.

Scheme II



(ii) Esters are produced, according to Scheme II, via the reaction of RO• with **4** (eq 13), while most of ketones are formed by the $^1O_2$ oxidation of **4** (eq 14). Therefore, the substituent effect on **4** for the formation of ester **6** might be different from that of ketone and then we examined it by a competitive experiment.


$$Ar(R)C{=}N_2 \;(\mathbf{4}) + R'O^{\bullet} \xrightarrow{-N_2} R{-}\overset{Ar}{\dot{C}}OR' \;(\mathbf{13}) \xrightarrow{O_2} \longrightarrow ArC(=O)OR' \;(\mathbf{6}) \quad (13)$$


$$\mathbf{4} + {}^1O_2 \xrightarrow{-N_2} Ar(R)C{=}\overset{+}{O}{-}O^- \xrightarrow{\mathbf{4}} 2\, ArC(=O)R \;(\mathbf{5}) \quad (14)$$

Thus, the photooxidation of a 1:1 mixture of *p*-$MeOC_6H_4(Et)CN_2$ (**4k**) and *m*-$NO_2C_6H_4(Me)CN_2$ (**4l**) gave two unscrambled esters, *p*-$MeOC_6H_4CO_2Et$ (**6k**) and *m*-$NO_2C_6H_4CO_2Me$ (**6l**), and two crossed ones, *p*-$MeOC_6H_4CO_2Me$ (**6m**) and *m*-$NO_2C_6H_4CO_2Et$ (**6n**), in addition to ketones *p*-$MeOC_6H_4COEt$ (**5k**) and *m*-$NO_2C_6H_4COMe$ (**5l**) as major products. The time courses of these products are shown in Figure 3. The formation of **5k** was about eight times faster than that of **5l** owing to the electron-donating *p*-MeO group, which is in line with the reported fact that $^1O_2$ reacts electrophilically with diazoalkanes.[46b] On the other hand, the ester ratios of $ArCO_2Et/ArCO_2Me$ (**6k**/**6m** and **6n**/**6l**) and *p*-$MeOC_6H_4CO_2R$/*m*-$NO_2C_6H_4CO_2R$ (**6k**/**6n** and **6m**/**6l**) were rather constant and only two as estimated from the initial stage of reaction. This result is consistent with an assumption of the reaction 13 as the ester formation if **4k** and **4l** have the same relative reactivity of ~2 toward both MeO• and EtO•. This seems to be reasonable since the substituent effect for the addition of alkoxyl radicals (eq 13) is probably much lower than the electrophilic $^1O_2$ oxidation (eq 14).

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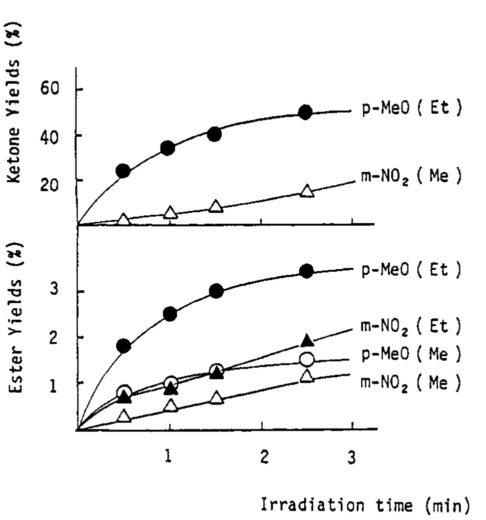


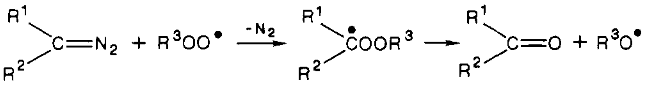
Figure 3. Time profiles for the formation of ketones and esters on the photooxidation of a 1:1 mixture (5.7 mM each) of p-$MeOC_6H_4(Et)CN_2$ (**4k**) and m-$NO_2C_6H_4(Me)CN_2$ (**4l**) in the presence of 0.2 mM TPP in MeCN-PhH (4:1). Irradiated at >400 nm under oxygen. Substituents of ketones and esters produced are shown simply as X(R) for XC_6H_4COR and $XC_6H_4CO_2R$, respectively.

All the results described above are consistent with the radical chain mechanism of Scheme II for the ester formation during the photooxidation of diazo compounds. Here, we should mention the participation of carbonyl oxides for the chain reaction. Their participation is apparent since the ester yields were reduced by the addition of methanol or sulfoxides as an efficient trapping agent for carbonyl oxides. Radical-like reactivities of the oxides, e.g., H-abstraction from hydrocarbons,[11,15a] are known and hence the chain decomposition of 4 may be initiated by radical species derived from carbonyl oxides. Alternatively, the oxide or its adduct with a diazo compound[47] may initiate the chain reaction.

Other points in Scheme II are discussed in the following. First, the present result indicates that alkoxyl radicals attack diazo compounds efficiently. This may be attributed to the nucleophilicity of the diazo carbon atom as well as the electrophilic alkoxyl radical. So far, only a few have been known about the addition of radical species to diazoalkanes.[48]

Second, most of carbon-centered radicals including α-hydroxyl alkyl and benzyl ones have been shown to react with oxygen at the almost diffusion-controled rate.[49] Thus, free radicals, **13** and **16**, generated under the oxygen-saturated or aerated conditions might be trapped efficiently by oxygen.

Third, peroxy radicals **14** and **17** add to diazoalkanes **4** to generate peroxyalkyl radicals **19** (eq 15). Peroxyalkyl



$$R^1R^2C{=}N_2 + R^3OO^\bullet \xrightarrow{-N_2} \underset{\mathbf{19}}{R^1R^2\dot{C}OOR^3} \longrightarrow R^1R^2C{=}O + R^3O^\bullet \quad (15)$$

radicals have been proposed in a chain decomposition of dialkyl peroxides and shown to fragment into ketones and alkoxyl radicals.[50]

Fourth, α-alkoxyl alkoxyl radicals $R^1R^2(R^3O)CO^\bullet$ such as **15** are known to decompose to esters and alkyl radicals.[51] It is reasonable to assume that the β-scission of **15**, promoted by the stability of ester formed,[52] proceeds efficiently to yield the alkyl radical and not the phenyl radical.

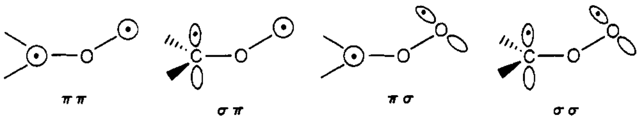
Thus the reaction sequence of Scheme II is quite reasonable. In fact, the ester/ketone ratio for the perester-initiated radical chain decomposition of **4b** (13 mM) was 0.33 and much higher than that (i.e., 0.06) for the photooxidation. This suggests that in the photooxidation about 20% of **4b** was decomposed via the radical chain decomposition. Here, the major reaction is the $^1O_2$ oxidation of diazomethanes to yield ketones as outlined in eq 14, since the quantum yields for the disappearance of 3.6, 8.3, and 16 mM **4a** were almost constant, i.e., 0.77, 0.75, and 0.94, respectively (TPP-sensitized in benzene under oxygen).

Barrier on the Cyclization of Carbonyl Oxides to Dioxiranes. Inconvertibility of carbonyl oxides **1** to more stable dioxiranes **2** in solutions, elucidated by this study, seems to disagree with the fact that **1** could be isomerized to **2** in the gas phase[25] or low temperature matrices.[6] However, the conflict is resolvable in that the isomerization arises from electronically or vibrationally excited states of **1** as discussed briefly in the following.

It has been revealed by several workers that in the gas phase "hot" or vibrationally excited carbonyl oxides are formed from primary ozonides and undergo unimolecular rearrangements or fragmentations.[23] Formation of such a "hot" molecule might not be expected in solutions because of rapid deactivation of the excess energy by solvents.

In low temperature matrices the irradiation of carbonyl oxides has been shown to give dioxiranes **2**[6d–h] and no scrambling of oxygens was observed in **2**.[6d] Therefore it is apparent that the dioxiranes are formed unimolecularly from the electronically excited state of **1** in the matrices. Such a two-photon process is improbable for the present TPP-sensitized photooxidation of **4** at room temperature because of the transient nature of **1**, i.e., too short life times.

We should search for a theoretical basis for the observed inconvertibility of carbonyl oxides to more stable dioxiranes. Theoretical studies indicated that carbonyl oxides in the ground state have a singlet biradical structure ($^1\pi\pi$) which is ~1 eV more stable than the corresponding triplet state ($^3\pi\pi$).[21b,f,j] The result is attributed to a significant interaction of localized spins between the carbon and terminal oxygen atoms through the lone pair of central oxygen (i.e., a so-called superexchange interaction). In fact, a relatively large overlap between the corresponding half-filled orbitals resulted from GVB[21b,f] and UHF[21g,j,m] calculations. The $\sigma\pi$ and $\pi\sigma$ states, formed by twisting the



orbitals around C–O and O–O bonds, were of ~1 and ~1.5 eV higher in energy, respectively, in comparison to the $^1\pi\pi$ state owing to break down of the stabilizing interaction.

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(47) (a) Conceivable biradical species are >$\dot{C}$N=NC(OO•)- or >$\dot{C}$N=NOOĊ<. It is notable that similar species may be formed by the reaction of azines with $^1O_2$ and initiate the chain oxygenation of azine.[47b] (b) Landis, M. E.; Madoux, D. C. *J. Am. Chem. Soc.* **1979**, *101*, 5106.

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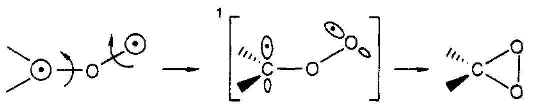
The isomerization of carbonyl oxides ($^1\pi\pi$) to dioxiranes must proceed via a $^1\sigma\sigma$-like transition state of higher energy (eq 16). Thus the observed inconvertibility of **1** to **2** in



1 ($^1\pi\pi$) transition state **2** (16)

solutions may be understood on the basis of the high activation energy required to break the stabilizing interaction between the localized spins (e.g., 23.9 kcal/mol at ab initio MCSCF level calculation[22b]) in spite of high exothermicity of the isomerization.

In conclusion, the unimolecular rearrangement of carbonyl oxides via dioxiranes in solutions as often proposed was ruled out clearly by ^{18}O-tracer experiments. The ester formation in the sensitized photooxidation of alkylphenyldiazomethanes was shown to proceed via a radical chain decomposition involving alkoxyl radicals as a chain carrier. For some particular cases, esters or anhydrides are formed by the Baeyer–Villiger oxidation of ketones produced with carbonyl oxide intermediates.

Experimental Section

^{1}H NMR spectra were recorded with a Hitachi R24B (60 MHz) or a JEOL GX-400 (400 MHz) NMR spectrometer. GLC analyses were performed with a Yanagimoto G180 gas chromatograph, using 2.5 mm × 1 m columns of PEG 20M, 10%, on Chromosorb WAW; Silicone OV-1, 3% on uniport HP; Dexsil 300GC, 2% on Chromosorb WAW. Shimadzu Chromatopac C-R1B and C-R3A integraters were used for quantitative analyses. GC-MS analyses were carried out with a JEOL D300 mass spectrometer using a 2.5 mm × 1 m column of ultrabond PEGS (Gasukuro Kogyo Inc.). Absorption spectra were recorded on a Hitachi ultraviolet spectrometer (Model 124) and a Shimadzu UV-265 spectrometer.

Materials. 1-Phenyldiazopropane (**4a**),[53] 1-phenyldiazoethane (**4b**),[53] 1,2-diphenyldiazoethane (**4c**),[54] 1,2-diphenyldiazopropane (**4d**),[55] phenyldiazomethane (**4e**),[53] diphenyldiazomethane (**4f**),[56] (trimethylsilyl)phenyldiazomethane (**4g**),[57] 7-diazo-8-acenaphthenone (**4f**),[58] and 1-(3-nitrophenyl)diazoethane (**4l**)[53] were prepared by the reported procedures. 1-(4-Methoxyphenyl)diazopropane (**4k**) was synthesized by the reported method for **4a**[53]: ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.23 (t, J = 7.0 Hz, 3 H), 2.50 (q, J = 7.0 Hz, 2 H), 3.78 (s, 3 H), 6.90 (s, 4 H).

Perdeuteriated 1-phenyldiazoethane (4b-d_8) was prepared by the reported method for **4b**[53] from acetophenone-d_8, which was obtained by the conversion of acetic acid-d_4 (CEA, 99.4% D) to acetyl chloride-d_3, followed by the Friedel–Crafts acetylation of benzene-d_6 (CEA, 99.6% D). The purity of **4b**-d_8 was measured from the mass spectrum of acetophenone-d_8 formed by the oxidation with $^1O_2$: 92.3 ± 0.6% D for methyl group and 99.2 ± 0.1% D for phenyl group.

Adamantanone azine (**7**)[59] and adamantylidenecyclopropane (**8**)[10a] were prepared according to the published procedures. Acetophenone diperoxide (**9b**, R_1 = Ph, R_2 = Me) was obtained from acetophenone and hydrogen peroxide according to the known method.[60] 3,4-Diphenyl-3-hexene (**11a**) was obtained as a mixture of isomers (cis/trans = 2/8) by a titanium-induced coupling of propiophenone.[61] Di-*tert*-butyl peroxyoxalate (**18**) was prepared as described in literature[46] and purified twice by recrystallization from hexane at low temperature: mp 50–51 °C (lit.[46] mp 50.5–51.5 °C). Oxygen gas $^{18}O_2$ (98.7% ^{18}O) was purchased from CEA and used after dilution with $^{18}O_2$. Ozone was generated by a Nippon Ozone 0-1-2 ozone generater and used as a mixture with oxygen containing 16.8 g/m^2 ozone.

Typical Procedure of the Photooxidation. A 3-mL benzene solution of 0.01 M ethylphenyldiazomethane (**4a**) and 0.01 mM tetraphenylporphine (TPP) in a 24-mL Pyrex tube was purged with oxygen and irradiated with a 300-W medium pressure Hg lamp through a 5% $NaNO_2$ filter solution (i.e., >400 nm) for 30 min at ca. 20 °C. The conversion of diazo compounds was usually complete in 10 min. Products were determined by GLC and identified by GC-MS analyses in comparison to authentic samples. No propiophenone diperoxide (**9a**) was detected by sensitive ^{1}H NMR analysis (400 MHz) with 128 times accumulation, i.e., <0.5%.

The results from various diazomethanes **4** are listed in Table II. Sometimes, the yields of esters were changed because of small amounts (<1%) of contaminated ketones and esters, formed by the autoxidation of **4**, in starting materials. The contaminated ketones and esters were determined after the complete consumption of diazoalkanes with dimethyl fumarate to obtain the exact values.

Photooxidation of Ethylphenyldiazomethane 4a in the Presence of MeOH. A similar procedure as described before[15a] showed the formation of 1-hydroperoxy-1-methoxy-1-phenylpropane, Ph(Et)C(OMe)OOH, in 30% yield. The hydroperoxide was purified by extraction with 0.1% NaOH, neutralization with AcOH, and extraction with CH_2Cl_2: ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.70 (t, J = 9 Hz, 3 H), 1.95 (q, J = 9 Hz, 2 H), 3.31 (s, 3 H), 7.38 (m, 5 H).

$^{18}O_2$-Tracer Study. A 3-mL benzene solution of 0.01 M **4a** and 0.1 mM TPP in a 20-mL Pyrex reaction vessel with a stopcock was degassed by repeated freeze–pump–thaw cycles, and a mixture of $^{16}O_2$ and $^{18}O_2$ ($^{16}O_2$:$^{16-18}O_2$:$^{18}O_2$ = 100:(1.17 ± 0.02):(27.9 ± 0.1)) was introduced with a gas pressure of 50–200 mmHg. After irradiation (>400 nm) for 30 min at ca. 20 °C, the content of ^{18}O in the ethyl benzoate (**6a**) formed was analyzed by GC–MS spectroscopy from the relative peak heights at m/e 136 (M), 138 (M + 2), and 140 (M + 4). The results obtained similarly from **4a**, **4b**, and **4e** are summarized in Table III.

The tracer experiments for **4g**, **4h**, **7**, and **8** were performed more conveniently as follows: A 3-mL solution of the starting material (3–10 mM) and TPP (0.1 mM) in a 4-mL Pyrex tube capped with a rubber septum (Aldrich) was purged with argon for 10 min, and 1.5 mL of oxygen gas ($^{16}O_2$:$^{16-18}O_2$:$^{18}O_2$ = 100:(0.62 ± 0.04):(8.35 ± 0.22)) in a syringe was introduced under 1 atm of pressure by sucking out an equal volume of solution using another syringe. Irradiations and product analyses were carried out as described above.

The ^{18}O content of trimethylsilyl benzoate (**6g**) could not be obtained simply from M + 2 and M + 4 values because the protonation of **6g** in the mass chamber led to a significantly enhanced M + 1 peak. So we compared observed values with an authentic sample and calculated the ^{18}O contents for retention and scramble pathways (Table IV). Other data for **4h**, **7**, and **8** are summarized in Table V.

Determination of Gas Evolved during the Photooxidation of 4h. The relative sensitivity of N_2O/N_2 on the mass spectroscopy at the ionizing voltage of 20 eV was determined to be 2.88 ± 0.05 from a mixture of authentic N_2 and N_2O gasses of known ratio. Nitrogen-free O_2 gas (260 mmHg) was introduced to a 10-mL degassed benzene solution of **4h** (10 mM) and TPP (0.1 mM) in an 18-mL Pyrex reaction vessel with a stopcock. After irradiation (>400 nm) for 1 h at ca. 20 °C, the solution was frozen at −78 °C and the gas phase was transferred to a direct gas inlet of the mass spectrometer. The resulting peak heights on mass spectrometry were 41.0 ± 2.5 and 97.8 ± 8.4 mm at m/e 28 (N_2) and 44 (N_2O), respectively. After the correction for relative sensitivity, the ratio of evolved N_2 and N_2O was determined, i.e., $N_2O/(N_2O + N_2)$ = 0.453 ± 0.044.

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Photooxidation of a Mixture of 4b and 4b-d_8. An oxygen-saturated MeCN-PhH (4:1) solution of **4b** (4.3 mM), **4b**-d_8 (4.3 mM), and TPP (0.1 mM) was irradiated similarly, and the isotope ratios of the resulting acetophenone (**5b**) and methyl benzoate (**6b**) were determined by mass spectrometry. For the ketone **5b**: M(m/e 120):(M + 6):(M + 7):(M + 8) = 100:(3.9 ± 0.4):(20.6 ± 1.2):(81.5 ± 6.8); i.e., **5b**-d_0:**5b**-d_6,d_7,d_8 = 1:(1.06 ± 0.08). On the other hand, for the ester **6b**, M(m/e 136):(M + 1):(M + 2):(M + 3):(M + 4):(M + 5):(M + 6):(M + 7):(M + 8) = 100:(12.1 ± 0.5):(17.5 ± 0.7):(83.9 ± 3.8):(10.7 ± 1.1):(92.5 ± 7.2):(11.6 ± 0.9):(21.5 ± 2.0):(84.1 ± 7.4). After a correction of ^{13}C (8.7%) contained in **6b**, deuterium contents in **6b** are d_0:d_1:d_2:d_3:d_4:d_5:d_6:d_7:d_8 = 100:3.4:17.2:82.4:3.5:92.2:3.6:21.2:82.3; i.e., **6b**-d_0:**6b**-d_1,d_2,d_3:**6b**-d_4,d_5:**6b**-d_6,d_7,d_8 = 1:(1.03 ± 0.05):(0.96 ± 0.08):(1.07 ± 0.10). Therefore, methyl and phenyl groups in **6b** were completely scrambled each other.

Quantum Yields. The quantum yields for the decrease of **4a** on the photooxidation were determined as described previously[62] by using a 150-W Xenon lamp and a monochrometer. The incident photoflux was 6.1 × 10^{-7} E/min at 405 ± 5 nm, and the decrease of 4a was monitored by absorption spectroscopy (**4a**, λ_{max} 515 nm, ϵ 38).

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Fluoride Ion Catalyzed Reduction of Aldehydes and Ketones with Hydrosilanes. Synthetic and Mechanistic Aspects and an Application to the Threo-Directed Reduction of α-Substituted Alkanones

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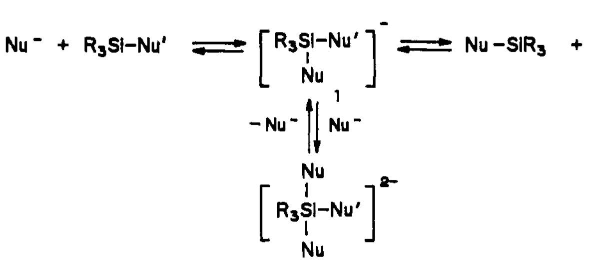
Reduction of aldehydes and ketones with hydrosilanes proceeded in the presence of a catalytic amount of tetrabutylammonium fluoride or tris(diethylamino)sulfonium difluorotrimethylsilicate in aprotic polar solvents under mild conditions. A significant isotope effect (k_H/k_D = 1.50) was observed in competitive reduction of acetophenone with $HSiMe_2Ph$ and $DSiMe_2Ph$. The reaction was of first order in the concentration of an aprotic polar solvent HMPA. Reduction of 2-methylcyclohexanone gave *cis*-2-methylcyclohexanol with selectivities up to 95%. The kinetic and stereochemical results suggest that a hexavalent fluorosilicate $[HSiR_3F(HMPA)]^-$ is involved. α-Alkoxy (acyloxy or dimethylamino) ketones were transformed to threo alcohols in high diastereoselectivities. The reduction was also applied to α-methyl-β-keto amides, $RCOCH(MeCONR)_2$, to afford the corresponding threo alcohols in >98% selectivity. The threo selectivity is explained in terms of the Felkin-Anh model in which interaction of carbonyl oxygen with a countercation is ideally suppressed. The threo-directed reduction was applied to (*R*)-1-phenyl-4-(2-tetrahydropyranyloxy)-1-penten-3-one and *N*-(2-benzoylpropanoyl)piperidine. The resulting threo alcohols were respectively converted into (2*R*,3*S*)-2,3-(cyclohexylidenedioxy)butanal, a key intermediate of daunosamine synthesis, and into a pharmacologically useful compound *threo*-*N*-(3-hydroxy-2-methyl-3-phenylpropyl)piperidine.

Stereochemistry in substitution reactions at silicon has been extensively studied recently, and these reactions were proved to proceed via penta- or hexacoordinated silicate intermediates (eq 1).[1] Fluoride ion as the nucleophile (Nu), in particular, forms a strong Si-F bond (595 kJ/mol)[2] upon the reaction with R_3Si-Nu and thus readily generates nucleophilic species fluorosilicate 1 (Nu = F) and/or Nu′$^-$. This reaction was first applied to organic synthesis by Corey, who succeeded in selective deprotection of silyl ethers under mild conditions by means of fluoride ion.[3] Kuwajima and Noyori extended the concept independently to the generation of naked enolates.[4] Later, the organosilane/F$^-$ system was demonstrated to be effective as well for the formation of various carbon nucleophiles including acetylides[5] and allyl anions[6] and has been frequently employed in current organic synthesis.[7]



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