2-necked, 100-mL, round-bottomed flask flushed with argon was charged with a solution of 4.54 g (11.52 mmol) of vinyl iodide **46b** in 35 mL of dry THF and cooled to −78 °C. *sec*-Butyllithium (16.6 mL, 23.04 mmol, 1.39 M in cyclohexane) was added via gas-tight syringe, and the resulting solution was allowed to stir at −78 °C for 1 h to give a cloudy orange solution. The reaction mixture was warmed to −40 °C, and transferred by cannula under nitrogen pressure into an oven-dried, 100-mL, round-bottom flask charged with 1.13 g (12.67 mmol) of CuCN. The resulting solution was allowed to stir at −40 °C for 2 h, during which time it became brown and then black in color. Bromoallene **47**[16] (2.34 g, 11.52 mmol) was added, and the reaction mixture was warmed to −20 °C and stirred for 27 h. The reaction mixture was quenched with 100 mL of 4:1 saturated $NH_4Cl:NH_4OH$, the blue aqueous solution was extracted 3 times with 100 mL of ether, and the organic solution was worked up to give 5.2 g of brown liquid. The crude product was purified by chromatography (hexane then 5% ether–hexane) to give 3.25 g (72% yield) of **48** as a colorless liquid: R_f 0.20 in hexane; IR 2940, 1460, 1250, 1090 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6), 0.89 (s, 9), 0.67–1.06 (m, 3), 1.06–1.79 (m, 19), 1.57 (s, 3), 1.79–1.95 (m, 1), 2.16 (m, 1), 2.60 (d, 1, J = 12.0), 2.87 (d, 1, J = 5.8), 3.16 (ddd, 1, J = 3.6, 8.9, 8.9), 5.14 (t, 1, J = 6.7); MS, m/e (relative intensity) 333 (0.06), 255 (0.36), 225 (0.34), 213 (2.63), 195 (1.61), 185 (0.38), 169 (1.24); HRMS calcd for $C_{25}H_{46}OSi$ 333.2615, found 333.2615.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (grant no. GM-30141). We also thank Professor W. C. Still for discussions of related work from his laboratories.

Registry No. **8** ($R = R^2 = CH_3$, $R^1 = CH_2OH$) (silyl ether), 101859-23-8; **8** ($R = R^1 = H$, $R^2 = CO_2Me$) (silyl ether), 101859-28-3; **8** ($R = R^2 = H$, $R^1 = CO_2Me$) (silyl ether), 101976-92-5; **8** (R = H, $R^2 = CH_3$, $R^1 = CH_2OCH_2Ph$) (silyl ether), 101859-32-9; **8** ($R = CH_3$, $R^1 = R^2 = H$), 101859-19-2; **8** ($R = CH_3$, $R^1 = R^2 = H$) (silyl ether), 101859-20-5; **8** (R = H, $R^2 = CH_3$, $R^1 = CO_2Me$) (silyl ether), 101859-22-7; **8** (R = H, $R^1 = CH_2OCH_2$-2,6-$Cl_2C_6H_3$, $R^2 = CH_3$) (silyl ether), 101859-33-0; **8a**, 101859-25-0; **8a** (silyl ether), 101859-24-9; **8b**, 101858-79-1; **8c**, 101858-81-5; **8c** (silyl ether), 101859-30-7; **8d**, 54363-09-6; **8e**, 101859-57-8; **8f**, 101858-84-8; **8g**, 96502-30-6; **8g** (silyl ether), 101859-34-1; **9b**, 101858-80-4; **9c**, 101858-82-6; **9d**, 101858-83-7; **9f**, 101858-85-9; **9g**, 101858-86-0; **10a**, 101858-87-1; **10c** (isomer 1), 101858-88-2; **10c** (isomer 2), 101858-89-3; **11a-F**, 101858-90-6; **11b-F**, 101858-91-7; **11b-H**, 101858-92-8; **11c-F**, 101858-93-9; **11c-H**, 101858-94-0; **11d-A**, 101858-95-1; **11g-F**, 101858-96-2; **11g-H**, 101858-97-3; **12d-A**, 101915-77-9; **17** (R = H), 3392-93-6; **17** (R = H) (silyl ether), 101859-35-2; **17** (R = H) (*p*-bromobenzyl ether), 101859-45-4; (*Z*)-**17** ($R = CO_2Me$) (silyl ether), 101859-37-4; (*Z*)-**17** ($R = CO_2Me$) (*p*-bromobenzyl ether), 101859-47-6; (*E*)-**17** ($R = CO_2Me$) (silyl ether), 101976-93-6; (*E*)-**17** ($R = CH_2OTHP$) (silyl ether), 101859-40-9; (*E*)-**17** ($R = CH_2OTHP$), 101859-41-0; (*E*)-**17** ($R = CH_2OTHP$) (benzyl ether), 101859-42-1; (*E*)-**17** ($R = CH_2OTHP$) (2,4-$Cl_2C_6H_3CH_2$ ether), 101859-49-8; **21**, 101858-98-4; **21** (silyl ether), 101859-38-5; **22**, 101858-99-5; **23**, 101859-00-1; **24** ($R = CH_2OH$) (A = 2,4-$Cl_2C_6H_3CH_2$, 101859-50-1; **24** (R = H) (A = CH(*p*-ClC_6H_4)2), 101859-52-3; (*Z*)-**24** ($R = CO_2Me$) (A = CH(*p*-$ClC_6H_4)_2$), 101859-54-5; (*Z*)-**24** ($R = CH_2OH$) (A = Si(Bu-*t*)Me_2), 101976-95-8; (*E*)-**24** ($R = CH_2OH$) (A = Si(Bu-*t*)Me_2), 101859-39-6; (*E*)-**24** ($R = CH_2OH$) ($A = CH_2Ph$), 101859-43-2; (*E*)-**24** ($R = CH_2OH$) (A = *p*-$BrC_6H_4CH_2$), 101859-48-7; (*E*)-**24** ($R = CH_2OH$) (A = CH(*p*-$ClC_6H_4)_2$), 101859-55-6; (*E*)-**24** ($R = CO_2Me$) (A = CH(*p*-$ClC_6H_4)_2$), 101976-94-7; (*E*)-**24** ($R = CO_2Me$) (A = *p*-$BrC_6H_4CH_2$), 101976-96-9; **29a**, 101859-44-3; **29b**, 101859-01-2; **29c**, 101859-51-2; **29d**, 101859-56-7; **30**, 101859-02-3; **31**, 101859-03-4; **32a**, 101859-05-6; **32b**, 101859-06-7; **33**, 101859-04-5; **34-F**, 101976-90-3; **34-H**, 101859-07-8; **35**, 101859-10-3; **35** (silyl ether), 101859-09-0; **36**, 101915-78-0; **37**, 101859-11-4; **38**, 101859-12-5; **39**, 101859-13-6; **40**, 101859-14-7; **41**, 101859-15-8; **42**, 101859-27-2; **43**, 101859-36-3; **43** (bromobenzyl ether), 101859-46-5; **43** (bis(chlorophenyl)methyl ether), 101859-53-4; **44**, 101859-16-9; **44** (silyl ether), 101859-17-0; **46b**, 101859-18-1; **47**, 75101-95-0; **48**, 101859-08-9; $Ph_3P{=}CHCO_2Me$, 2605-67-6; $Ph_3P{=}CHCH_2CO_2Me$, 40955-14-4; $(F_3CCH_2)_2O_3PCH_2CO_2Me$, 88738-78-7; bis(4-chlorophenyl)methyl bromide, 6306-46-3; 3-chloro-2-methyl-1-propene, 563-47-3; cyclohexene oxide, 286-20-4; 1-((1*R**,2*S**)-2-((*tert*-butyldimethylsilyl)oxy)cyclohexyl)-2-propanone, 101859-21-6; (1*R**,2*S**)-2-hydroxycyclohexane acetonitrile, 101976-91-4; (1*R**,2*S**)-((2-*tert*-butyldimethylsilyl)oxy)cyclohexaneacetonitrile, 101859-26-1; (2E_1(1*R**,2*S**))-4-(2-((*tert*-butyldimethylsilyl)oxy)cyclohexyl)-2-buten-4-ol, 101859-29-4; (1*R**,2*S**,(2*E*))-2-((*tert*-butyldimethylsilyl)oxy)cyclohexane-3-methyl-2-buten-4-ol, 101859-31-8; 2,6-dichlorobenzyl bromide, 20443-98-5; 2,4-dichlorobenzoyl bromide, 89-75-8; 4-bromobutene, 5162-44-7; brevetoxin B, 79580-28-2.

Supplementary Material Available: Experimental details for the synthesis and characterization of the cyclization substrates (23 pages). Ordering information is given on any current masthead page.

Metalloporphyrin-Catalyzed Decomposition of Cyclic Diperoxides (1,2,4,5-Tetraoxanes)

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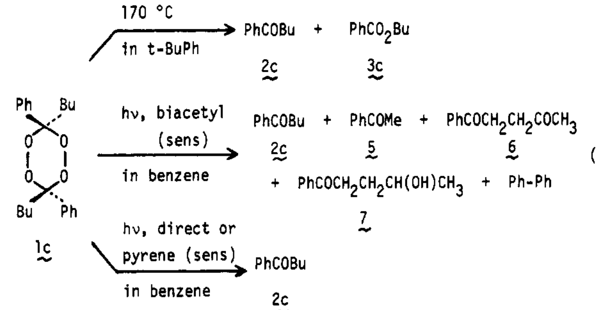
Cyclic diperoxides of type **1** (**a**, R = H; **b**, R = Ph; **c**, R = *n*-Bu; **d**, R = Me) were found to be very stable (E_a = 42–48 kcal/mol, log A = 17–19). Decomposition of **1** was greatly promoted by addition of ZnTPP or CoTPP, leading to formation of ketone PhCOR and ester (or acid) $PhCO_2R$ as the major products. In the presence of Ph_2S or Ph_2SO as oxygen acceptor, the oxygen transfer reaction occurred and the production of $PhCO_2R$ (= $PhCO_2Bu$) was completely suppressed in the case of **1c**, while it (the production of $PhCO_2H$) was not measurably suppressed in the case of **1a**. Chemiluminescence (CL) that is due to singlet ZnTPP formation was detected from the reaction of ZnTPP with **1a** but not with **1c**. The observed first-order decay rate of CL for the reaction of **1a** with ZnTPP and its para-substituted derivatives Zn(*p*-X)TPP increased with the increase in electron-donating nature of the substituents ($CN < Cl < H < CH_3 < OCH_3$). A tentative mechanism for this ZnTPP-catalyzed decomposition reaction, which takes the different behaviors of **1a** and **1c** into account, is proposed.

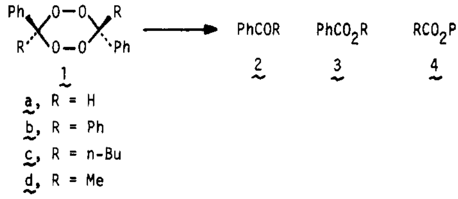
Decomposition of valerophenone diperoxide (**1c**) has previously been performed thermally and photochemically under a nitrogen atmosphere (eq 1).[1,2] The primary reaction observed was the formation of (a) valerophenone



(1)

(**2c**) (47%) and butyl benzoate (**3c**) (4%) upon thermolysis (170 °C) in *tert*-butylbenzene,[1] (b) **2c** (29%), acetophenone (**5**) (33%), 1-phenylpentane-1,4-dione (**6**) (13%), γ-hydroxyvalerophenone (**7**) (8%), and biphenyl (10%) upon biacetyl triplet-sensitized photolysis in benzene ([biacetyl] = 0.46 M),[2] and (c) only **2c** upon direct photolysis or pyrene singlet-sensitized photolysis in benzene.[2] Compounds **6** and **7** were produced only by biacetyl sensitization and are assumed to be from the decomposition of **1c** in a solvent cage.[2] This was further supported by the finding that, when the biacetyl-sensitized photolysis (biacetyl 0.46 M in benzene) was carried out at high temperature (93 °C) instead of at room temperature, the yield for **6** and **7** decreased drastically: **2c** (47%), **5** (7%), **6** (1%), **7** (0.3%), and biphenyl (7%).[3] Acetophenone (**5**), which was formed in a remarkably high yield by the biacetyl sensitization, was probably formed via a Norrish type II biradical without going through triplet valerophenone.[2]

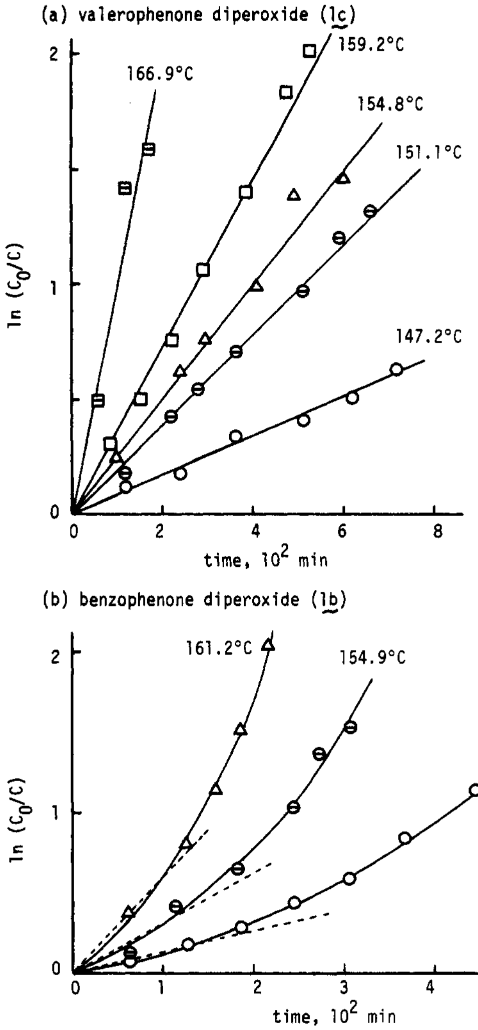
Metalloporphyrins are known to catalyze the decomposition of some peroxides and this reaction has biological significance.[4,5] Since cyclic diperoxides of type **1** are interesting molecules in view of their structure as a dimer of carbonyl oxide or dioxirane, it is attractive to study the metalloporphyrin-catalyzed decomposition of **1**. Those experiments are reported herein.



(2)

Results and Discussion

(1) Arrhenius Parameters for Thermolysis of 1. Thermolysis of **1a** (R = H), **1b** (R = Ph), **1c** (R = *n*-Bu), and **1d** (R = Me) in diphenyl ether was carried out at several temperatures under nitrogen. The disappearance of **1** was monitored by HPLC in each case. The decomposition of the diperoxides **1a**, **1c**, and **1d** obeyed a first-order kinetic law as shown in Figure 1a (where only the result for **1c** is depicted). The activation parameters are summarized in Table I. Although the first-order plot for the decomposition of **1b** did not give a straight line (Figure 1b), its activation parameters were estimated (Table I) from the initial rates which were approximated by dotted lines as drawn in Figure 1b. Catalysis by reaction products is one of the possible explanations for this nonlinear first-order plot.



	10^5k, s^{-1}
(a)	
166.9°C	17.0
159.2	5.9
154.8	4.3
151.1	3.3
147.2	1.4
(b)	
161.1	10.6
154.9	5.7
150.0	2.9

Figure 1. Plot of ln (C_0/C) vs. time for the thermal decomposition of valerophenone diperoxide (**1c**) and benzophenone diperoxide (**1b**), where C_0 is the initial concentration of **1c** or **1b**. Reaction conditions: solvent, diphenyl ether; temperature, ±0.2 °C; $C_0 \sim 10^{-2}$ M.

Table I. Activation Parameters for Thermolyses of Cyclic Diperoxides 1 in Diphenyl Ether

cyclic diperoxide	E_a, kcal/mol[a]	log A[b]
1a, R = H	48	19
1b, R = Ph	42	17
1c, R = *n*-Bu	44	18
1d, R = Me	47	18

[a] ±2 kcal/mol. [b] ±2; A in s^{-1}.

In general, cyclic diperoxides of type **1** are very stable.[6] As expected, the diperoxides **1a–d** have high activation energies (E_a = 42–48 kcal/mol). The values for log A (= 17–19) appear to be too large for an unimolecular decomposition,[7] but the reason for this is at present unclear.

(2) MTPP-Catalyzed Decomposition of 1. Thermolyses of the diperoxides **1a–c** in the presence of *meso*-

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[4] (a) Boyd, J. D.; Foote, C. S.; Imagawa, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 3641. (b) Balci, M.; Sutbeyaz, Y. *Tetrahedron Lett.* **1983**, *24*, 311. (c) Yuan, L.-C.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 512. (d) Lee, W. A.; Bruice, T. C. *Ibid.* **1985**, *107*, 513.

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[6] (a) McCullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L. *J. Chem. Res., Synap.* **1980**, 35. (b) Cafferata, L. F. R.; Eyler, G. N.; Mirifico, M. V. *J. Org. Chem.* **1984**, *49*, 2107.

[7] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 134.

Table II. Thermal Decomposition of Cyclic Diperoxides 1a–c in the Presence of Metalloporphyrin MTPP[a]

cyclic diperoxide (mM)	MTPP (mol %)[b]	solvent	decomposition temp, °C	decomposition time, h	products (%) 2	3	4	5	6	convrsn of 1 (%)
1a (200)	Zn (7.2)	$CHCl_2CHCl_2$	90	10	67	33	*c*			100
1a (200)	Co (7.2)	$CHCl_2CHCl_2$	90	10	59	40	*c*			100
1a (17)	Zn (18)	PhOPh	90	5.5	53	43	*c*			100
1a (15)	none	PhOPh	170	4	59	31	*c*			100
1b (13)	Zn (12)	$CHCl_2CHCl_2$	130	10	93	7				100
1b (13)	Co (12)	$CHCl_2CHCl_2$	130	10	84	16				100
1b (13)	Zn (12)	*t*-BuPh	130	10	93	7				100
1b (13)	Co (12)	*t*-BuPh	130	10	100	0				100
1c (210)	Zn (7.2)	$CHCl_2CHCl_2$	130	10	97	2	0	*c*	*c*	56
1c (210)	Co (7.2)	$CHCl_2CHCl_2$	130	10	71	11	trace	*c*	*c*	86
1c (210)	Zn (7.2)	*t*-BuPh	130	10	91	8	trace	0	*c*	55
1c (210)	Co (7.2)	*t*-BuPh	130	10	90	9	trace	0	*c*	95
1c (290)	none	*t*-BuPh	170	4	47	4	*c*	0.19	*c*	100
1c (110)	none	PhOPh	172	1.7	43	14	1	0.52	0[d]	74

[a] All yields for the products appearing in this paper were calculated on the basis of an expected 2 mol of each from 1 mol of cyclic diperoxide 1. [b] Relative to cyclic diperoxide 1. [c] Not measured. [d] In a separate experiment 2-phenoxybiphenyl was isolated in 16% yield.

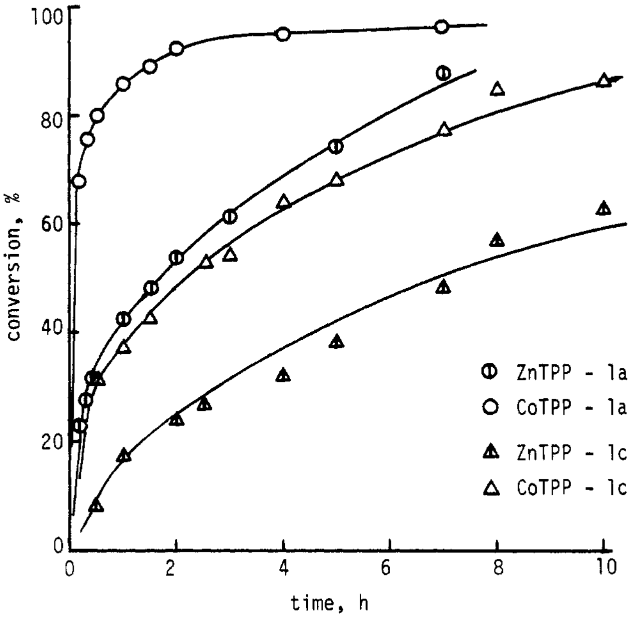

Figure 2. Reaction of cyclic diperoxides **1a** and **1c** with MTPP: conversion of **1a** and **1c**. Reaction conditions: solvent, $CHCl_2CHCl_2$; temperature, 130 ± 3 °C; [1] ~ 0.2 M; [MTPP] = 3.6 mol % relative to **1a** or 10 mol % relative to **1c**.

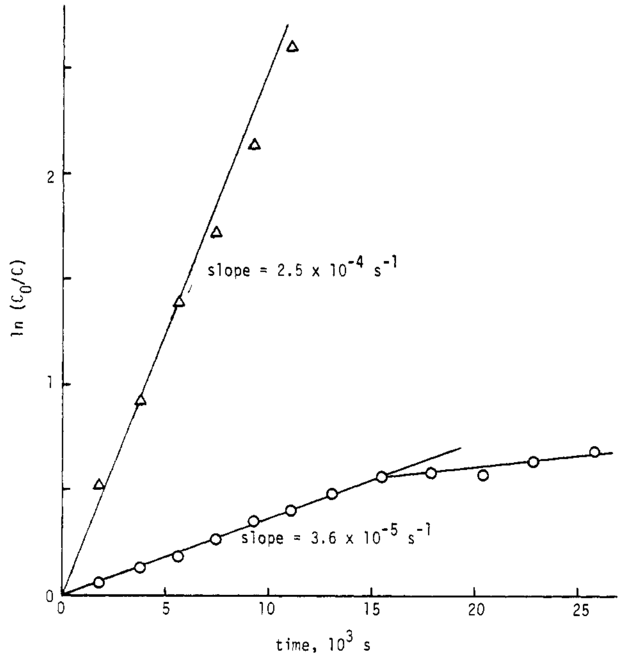

Figure 3. Plot of ln (C_0/C) vs. time for the thermal reaction of benzaldehyde diperoxide (**1a**) with ZnTPP at 80.7 ± 0.1 °C, where C_0 is the initial concentration of **1a** (6.0×10^{-3} M) or ZnTPP (5.6×10^{-4} M) in diphenyl ether: **1a** (○), ZnTPP (△).

tetraphenylporphine metal complexes MTPP (ZnTPP and CoTPP) were carried out in diphenyl ether, *tert*-butylbenzene, or 1,1,2,2-tetrachloroethane as solvent.[8] The thermolyses were done under a nitrogen atmosphere. However, it was found independently that the reaction was almost insensitive to the presence of air. The progress of the reaction is illustrated in Figure 2 (for **1a** and **1c** at 130 °C) and in Figure 3 (for **1a** at 80.7 °C).

More than 50% of **1a** and **1c** decomposed in less than 8 h at 130 °C (Figure 2). The rate of decomposition for **1a** was significant even at 80.7 °C ($1/k$ = 7.7 h, Figure 3). On the basis of the data in Table I, the periods of half decay ($t_{1/2}$) for **1a** and **1c** at 130 °C are, respectively, 1400 h and 100 h. **1a** is virtually unreactive at 81 °C ($t_{1/2} = 5 \times 10^6$ h). It is clear that the decomposition of these peroxides is dramatically promoted by MTPP. However, MTPP was also decomposed during the reaction. As the slopes in Figure 3 demonstrate, ZnTPP disappeared about 7 times faster than **1a**. Inspection of Figures 2 and 3 suggests that peroxide **1** is easily decomposed in the presence of MTPP but a slower degradation of **1** continues even after complete consumption of MTPP.

Table II contains a summary of the product distributions for the MTPP-catalyzed decomposition of the diperoxides **1a–c**. Major products are the corresponding ketone **2** and acid (or ester) **3** as in the thermal decomposition in the absence of MTPP.[1,6,10] A MTPP-catalyzed decomposition of **1c** leading to acetophenone (**5**) formation was not observed, in contrast to the biacetyl-sensitized photolysis.[2]

(3) Oxygen Transfer Reactions. Carbonyl oxide and dioxirane can transfer the oxygen atom in their molecules to other organic substrates.[11] It is worthwhile to see

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[8] The reaction in a dioxane solution was very slow, probably as a result of coordination of dioxane to MTPP.[9]

[9] Vogel, G. C.; Stahlbush, J. R. *Inorg. Chem.* **1977**, *16*, 950.

[10] According to the general scheme presented previously,[6] products derived from radicals R· or Ph· should be formed. We did not, however, search for such products. Production of the solvent-derived products, i.e., biphenyl and 2-phenoxybiphenyl from biacetyl-sensitized photolysis of 1c in benzene[2] and from thermolysis of 1c in diphenyl ether (footnote d in Table II), respectively, may be indicative of Ph· formation in these reactions. Obviously, the benzene solvent participates in the production of biphenyl, since it was not detected when the reaction was carried out in hexane.

Table III. MTPP-Catalyzed Thermolysis of Cyclic Diperoxides 1a and 1c in the Presence of Oxygen Trapping Reagent[a,b]

cyclic diperoxide	acceptor	MTPP	decomposition		products, %		
			temp, °C	time, h	2	3	others
1a	Ph_2S	Zn	90	10	49	41	27 Ph_2SO
		Co	90	10	55	35	37
1a	Ph_2SO	Zn	90	10	35	45	2 Ph_2SO_2
		Co	90	10	45	33	14
1c	Ph_2S	Zn	130	10	76	0	10 Ph_2SO
		Co	130	10	64	0	7
1c	Ph_2SO	Zn	130	10	69	0	15 Ph_2SO_2
		Co	130	10	65	0	11

[a] A $CHCl_2CHCl_2$ solution containing either 1a (55 mM), MTPP (2 mM) and the acceptor (550 mM) or 1c (28 mM), MTPP (2.8 mM), and the acceptor (280 mM) was subjected to thermolysis. [b] See footnote a in Table II.

Table IV. Total Chemiluminescence Yield Φ_{CL} from the Reaction of 1a with ZnTPP in Diphenyl Ether

1a, mM	ZnTPP, mM	temp, °C[a]	Φ_{CL}, einstein/mol[b]
5.86	0.583	81.6	1.4×10^{-5}[c]
5.86	0.583	90.6	1.5×10^{-5}[c]
5.86	0.583	90.6	1.4×10^{-5}[d]
0.440	0.0175	87.7	3.8×10^{-5}[c]

[a] ±0.4 °C. [b] Calculated based on the amount of ZnTPP employed. [c] Under air. [d] Degassed by four freeze-pump-thaw cycles before CL measurement.

whether cyclic diperoxide 1 has similar oxygen transfer properties. MTPP-catalyzed decomposition of 1a in the presence of diphenyl sulfide (nucleophilic oxygen acceptor[12]) or diphenyl sulfoxide (electrophilic oxygen acceptor[12]) produced Ph_2SO and Ph_2SO_2, respectively, as well as the appropriate ketone **2a** and acid **3a** (Table III). The same oxygen transfer reactions occurred for **1c**. It is noticeable, however, that in the latter case production of ester **3c** is completely suppressed by the addition of the acceptors (compare Table II and Table III).

(4) Chemiluminescence from 1a and ZnTPP. Chemiluminescent reactions of metalloporphyrins and hydroperoxides involving the excited singlet metalloporphyrin[5a–c] or singlet oxygen[5d] as the chemiluminescence (CL) emitter have been known for a long time. Benzophenone diperoxide (**2b**) is reported to give weak direct and indirect CL.[13] Although we could not detect CL from the ZnTPP-catalyzed decomposition of **1b** and **1c** with the instrument at Kyoto University, it was easily detectable from the reaction of **1a** and ZnTPP above 70 °C in various solvents (diphenyl ether, *tert*-butylbenzene, and 1,1,2,2-tetrachloroethane). The CL spectrum (λ_{max} ~600 and 640 (shoulder) nm) was very similar to the ZnTPP fluorescence under similar conditions. (CoTPP is nonfluorescent[14] and no CL was observed from **1a** and CoTPP.) The CL decay rate was almost equal to the rate for disappearance of ZnTPP which was determined by HPLC. The CL was invisible in a dioxane solution.[8] It was also invisible when free base TPP was used instead of ZnTPP. Singlet oxygen is not generated as a result of reaction of **1a** or **1c** with ZnTPP, since the 1270-nm emission from $^1O_2$ was undetectable from the reaction solution with a germanium photodiode.[15]

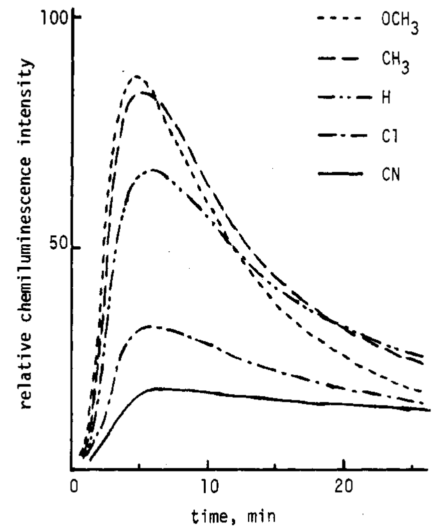

Figure 4. Chemiluminescence decay curve for the reaction of benzaldehyde diperoxide (**1a**) with Zn(*p*-X)TPP at 90 °C in 1,1,2,2-tetrachloroethane: [1a] = 1×10^{-2} M, [Zn(*p*-X)TPP] = 1×10^{-3} M.

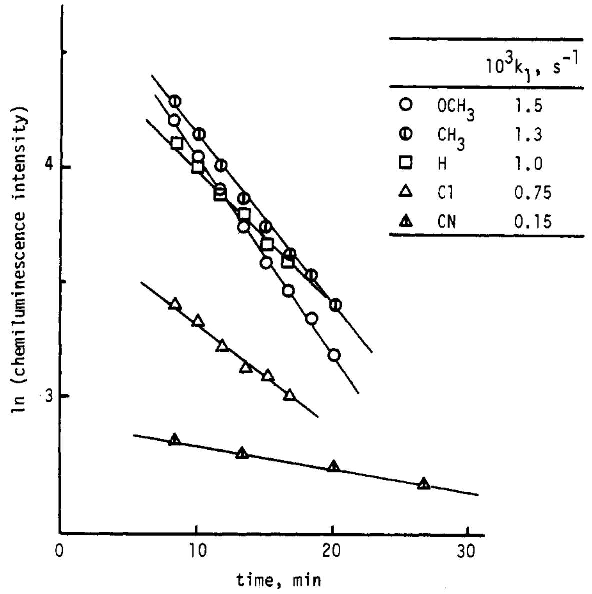

Figure 5. First-order plot of the chemiluminescence decay shown in Figure 4: k_1, the rate constant for the chemiluminescence decay.

The total CL yield Φ_{CL} (= the total CL intensity divided by the amount of ZnTPP employed) was measured and the result is summarized in Table IV. Φ_{CL} was essentially independent of oxygen concentration and was approximately 10^{-5} einstein/mol. Φ_{CL} was somewhat dependent on the concentrations of the reactants, probably because of an internal filter effect by ZnTPP. Since the fluorescence quantum yield of ZnTPP is about 0.03,[14] the efficiency of singlet ZnTPP formation from the reaction of **1a** and ZnTPP may be calculated to be around 0.1 %.

In order to examine the mechanism for this CL reaction, reactions of **1a** with a series of para-substituted *meso*-tetraphenylporphine zinc complexes Zn(*p*-X)TPP (X = OCH_3, CH_3, H, Cl, and CN) were tested. The results are described in Figures 4 and 5. After the time lag (ca. 8 min.)

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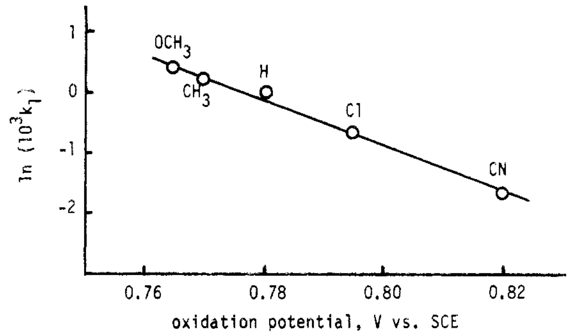
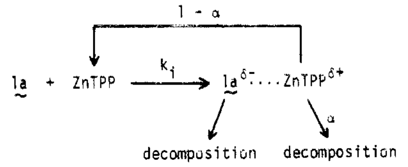


Figure 6. Correlation between $\ln k_1$ and the oxidation potentials of Zn(p-X)TPP.

that is required for thermal equilibration of the solution to 90 °C, the CL of each sample decayed smoothly as is shown in Figure 4. Figure 5 shows the first-order plots for these CL decays.

Judging from Figures 3 and 5, ZnTPP and its para-substituted derivatives appear to decompose initially with first-order kinetics as a result of reaction with a large excess of **1a**. Since the mechanism for the ZnTPP decomposition is probably complex, this result may be somewhat surprising. According to the assumed scheme represented by eq 3, where α is the probability of ZnTPP decomposition



(3)

from an intermediate with charge-transfer character (vide infra), the rate for disappearance of ZnTPP can be represented by eq 4. It is reasonable to consider the concentration of **1a** to be approximately constant during the initial stage of the reaction, since **1a** is present far in excess and the decomposition rate of ZnTPP is much greater than that of **1a** (Figure 3). These considerations explain the observed first-order decomposition of ZnTPP (eq 5).

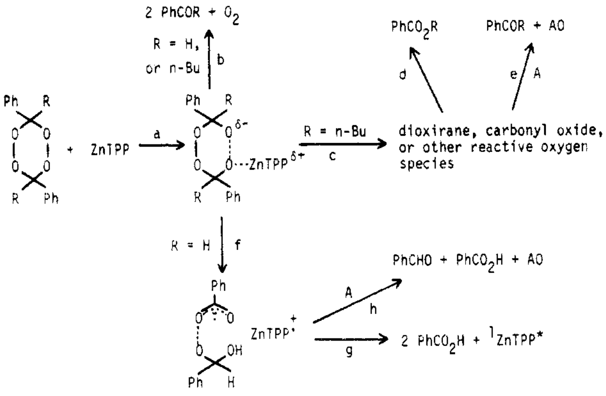
$$-d[\mathrm{ZnTPP}]/dt = \alpha k_1[\mathbf{1a}][\mathrm{ZnTPP}] \qquad (4)$$

$$-d[\mathrm{ZnTPP}]/dt \approx k_1[\mathrm{ZnTPP}] \qquad (5)$$

It is evident from Figure 5 that the CL decay rate (and hence the Zn(p-X)TPP degradation rate) increases with the electron-donating ability of the substituents (CN < Cl < H < CH_3 < OCH_3). As displayed in Figure 6, there is a good correlation between this rate and the oxidation potential ($E_{1/2}^{ox}$)[16] of Zn(p-X)TPP. ZnTPP is known to form complexes with neutral bases.[9] In the ZnTPP-catalyzed decomposition of certain peroxides, the metalloporphyrin is assumed to function as an electron donor.[5a-c] The linear relationship presently observed (Figure 6) supports this assumption. Presumably the role of CoTPP is similar to that of ZnTPP. As seen from Figure 2, the reaction of CoTPP is faster than that of ZnTPP and this fact is probably attributed to the lower oxidation potential of CoTPP (0.66 V) compared with that of ZnTPP (0.73 V).[17]

(5) Tentative Reaction Mechanism. We have revealed four mechanistic facts about the MTPP-catalyzed decomposition of **1**: (a) while the formation of $PhCO_2R$ (**3**) is completely suppressed by addition of the oxygen acceptors (Ph_2S and Ph_2SO) in the case of **1c**, it is not suppressed in the case of **1a**, (b) CL is observable from **1a** but not from **1c**, (c) ZnTPP decomposes with a first-order rate upon reaction with a large excess of **1a**, and (d) the Zn(p-X)TPP decomposition rate increases with the increase in electron-donating nature of the ring-substituent X. The first two results suggest that diperoxides **1a** and **1c** decompose with different mechanisms.

Scheme I



(A = Ph_2S or Ph_2SO)

A tentative reaction mechanism is described in Scheme I. The ability of a dioxirane or carbonyl oxide to transfer oxygen (step e) is known.[11] Step g is similar to the electron exchange luminescence mechanism of secondary peroxy esters.[18] Requirement of a C–H grouping adjacent to the peroxide bond for light emission (step f) is interesting, because it is reminiscent of the reaction mechanism for bacterial bioluminescence.[19] The expected facile hydrogen migration in this step (step f)[5b,c] is probably responsible for the larger catalytic effect of ZnTPP on the decomposition of **1a** compared with the effect on the decomposition of **1c**.

Experimental Section

Materials. Cyclic diperoxides (1,2,4,5-tetraoxanes) **1a–d** were prepared by the published methods.[1,20,21] *meso*-Tetraphenylporphine (TPP) and its para-substituted derivatives were prepared from the appropriate aldehyde and pyrrole in propionic acid according to the standard method.[22] The metal complexes (MTPP) were prepared by heating the proper metal salt ($Zn(OAc)_2 \cdot 2H_2O$ or $Co(OAc)_2 \cdot 4H_2O$) with the free base in dimethylformamide.[23]

Determination of Arrhenius Parameters. Solutions of cyclic diperoxides **1a–d** (10–20 mg, ~5 × 10^{-2} mmol) in diphenyl ether (0.5–1 mL), containing β-acetonaphthone (2–5 mg) as an internal standard for high performance liquid chromatography (HPLC) analyses, were maintained in a silicone oil thermostat at varied temperatures (135–176 °C, ±0.2 °C) under slow stream of nitrogen. The disappearance of **1a–d** was followed by HPLC (Finesil 5 silica gel column, hexane–ethyl acetate as eluent).

MTPP-Catalyzed Decomposition of 1a–c. A typical procedure is as follows. A solution of **1a** (100 mg, 0.41 mmol) and ZnTPP (20 mg, 0.03 mmol) in 2 mL of $CHCl_2CHCl_2$ was heated on an oil bath (90 ± 3 °C) for 10 h under bubbling nitrogen.

The reaction mixtures obtained as above or as in the next section were analyzed by HPLC (Finesil 5 silica gel column, hexane–ethyl acetate as eluent), using appropriately β-acetonaphthone (for **1a–c**, **2a–c**, **3a–c**, **4c**, **5**, Ph_2SO, Ph_2SO_2, and

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ZnTPP), benzophenone (for **1c**), or Ph_2SO_2 (for **3a**) as the internal standard. The compound **6** was analyzed by vapor phase chromatography (20% silicone DC 550 on Celite 545, 180 °C).

MTPP-Catalyzed Decomposition of 1a and 1c in the Presence of Oxygen Acceptor. Ten moles of the oxygen acceptor (Ph_2S or Ph_2SO) relative to the cyclic diperoxide was always employed. A typical procedure is as follows. A solution containing 20 mg (0.082 mmol) of **1a**, 2 mg (0.003 mmol) of ZnTPP, and 153 mg (0.82 mmol) of Ph_2S in 1.5 mL of $CHCl_2CHCl_2$ was heated on an oil bath (90 ± 3 °C) for 10 h under bubbling nitrogen. The reaction mixture was analyzed by HPLC as described above.

Chemiluminescence Measurement. Chemiluminescence (CL) was measured by a Shimazu RF-500 fluorescence spectrometer, with the emission bandwidth setting at 40 nm. The indirect CL from 9,10-dibromoanthracene and a 1,2-dioxetane derived from 2,3-diphenyl-1,4-dioxene (92.8 °C) was used as a standard of photon emission ($\Phi_*^T = 0.22$,[24a] $\Phi_F^{DBA} = 0.05$,[24b] $k_{ET}^{TS}/(k_{ET}^{TS} + k_{ET}^{TT}) = 0.2$,[24b] intercept/slope of the $1/I_{CL}$ vs. $1/[DBA]$ plot = 308 M^{-1} determined by us). Any corrections for the different spectral distribution of CL and the variable wavelength response of the photomultiplier tube (Hamamatsu R 446) were not made. The temperature of a sample solution (3 mL) was controlled by circulating hot water through the sample holder (±0.4 °C).

Isolation of 2-Phenoxybiphenyl. A solution of valerophenone diperoxide (**1c**) (269 mg, 0.755 mmol) in diphenyl ether (10 mL) was thermolyzed at 177 ± 5 °C for 5 h under bubbling nitrogen. The reaction mixture was separated by column chromatography on silica gel (Wakogel C-200, hexane), followed by preparative TLC (Merck Kieselgel 60 PF_{254}, hexane), to afford 59 mg (16% yield) of 2-phenoxybiphenyl as colorless oil. The product was identical with the authentic sample in every respect. Isolation of other products was not attempted in this run.

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A Two-Ring Flip as the Threshold Enantiomerization Route for a Triarylvinyl Propeller. 1D and 2D NMR and Static and Dynamic Stereochemistry of Trimesitylethylene

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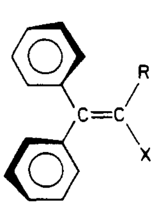
1,2,2-Trimesitylethylene (**16**) was prepared by dehydration of 1,2,2-trimesitylethanol. Its 1D ^1H and ^{13}C NMR spectra at room temperature show separate signals for pairs of groups (*o*-Me, *o*-C, *m*-C, and *m*-H) on the same ring, in agreement with a propeller conformation in solution. Assignment of the signals and derivation of the threshold rotational mechanism were aided by the use of 2D NMR techniques. Two rotational barriers were measured by dynamic NMR. The lower barrier (16.8 ± 0.1 kcal mol^{-1}) is for the threshold mechanism which is an $[\alpha,\beta]$-two-ring flip. The higher barrier was calculated for the interchange of diastereotopic groups on the β'-ring (20.5 ± 0.1 kcal mol^{-1}). The difference in the threshold mechanisms of **16** and of trimesitylethenol (a three-ring flip) was ascribed to the presence of the small hydrogen on **16** which allows the β'-ring cis to it to undergo a nonflip process in a transition state with an energy lower than that of the three-ring flip for **16** or the two-ring flip for trimesitylethenol. The distinct rotational threshold mechanisms for $Mes_2C{=}C(X)Mes$ (X = H, and OH, (Mes = mesityl)) are clearly reflected in their different 2D exchange NMR spectra.

1,1-Diarylvinyl (**1**) and 1,2,2-triarylvinyl systems **2** exist in a "propeller" conformation in which all the rings are twisted in the same sense[1–4] and are, therefore, the vinyl analogues of molecular propellers of the type Ar_3Z (**3**) and Ar_3ZX (**4**) (Z = C, B, or N; X = H, Me, or halogen).[5] When all the rings are identical and have a local C_2 axis, these systems exist as two enantiomers differing in the helicity, i.e., in the sense of twist of the rings.



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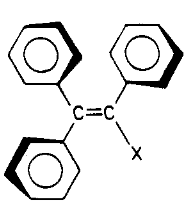

2

An important class of rotations in molecular propellers are correlated rotations in which all the rings rotate concomitantly. These processes are commonly analyzed in terms of "flip" mechanisms, each involving helicity reversal.[6] A "flip" of a ring is defined as its passage through a plane perpendicular to the reference plane (the double bond plane for 1 and 2[7] and the plane defined by the three

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[7] Note that for systems 1 and 2 (when R ≠ X) the molecules belong to the C_1 point group, and, therefore, the two double bond π faces reside in diastereotopic environments. For such olefins, deviation from the ideal planar arrangement should be expected. However, for simplifying the visualization of the different flip routes we will use the term "double bond plane".