Pergamon

Tetrahedron 55 (1999) 4287–4298

TETRAHEDRON

Synthesis of 3-Alkoxy-3-aryl-4,4-diisopropyl-1,2-dioxetanes and their Base-Induced Chemiluminescence

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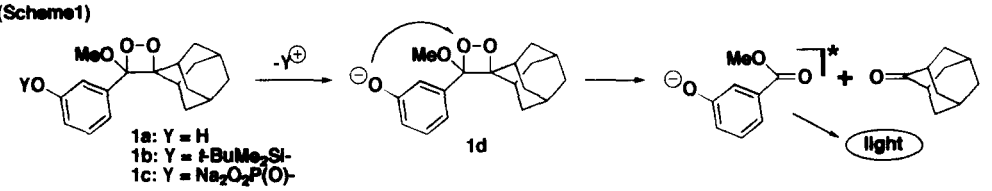
Received 24 December 1998; accepted 5 February 1999

Abstract: Low-temperature singlet oxygenation of 1-alkoxy-1-aryl-2,2-diisopropylethylenes (**9**) gives the corresponding 1,2-dioxetanes (**10**) in high selectivity. Dioxetanes (**10**) are thermally stable enough to permit handling at room temperature, though an alkoxy group affects significantly their thermal stability and the order of half-life is MeO < EtO < *i*-PrO >> *tert*-BuO. On treatment with tetrabutylammonium fluoride in DMSO, dioxetanes (**10e** - **10h**) bearing a *m*-siloxyphenyl decompose rapidly to emit intense blue light with $\Phi_{CL} > 0.2$. For the base-induced decomposition of **10e** - **10h**, the order of rate of decomposition is MeO < EtO < *i*-PrO < *tert*-BuO.

Keywords: singlet oxygenation, temperature effect, 1,2-dioxetane, chemiluminescence

High-energy molecules, 1,2-dioxetanes have received a great deal of attention because of their unique property to decompose thermally to electronically excited carbonyl products.[1-3] Thermolysis of rather simple dioxetanes generally leads mainly triplet-excited carbonyls so that only weak luminescence is observed. In contrast, dioxetanes bearing an aromatic electron donor have recently been found to display charge transfer induced decomposition affording light efficiently.[4-7] A representative case is dioxetanes (**1**) substituted with a *m*-hydroxyphenyl group or its protected form,[8] whose deprotonation or deprotection generates an unstable dioxetane (**1d**) bearing a phenoxide anion, from which a charge transfer occurs to the dioxetane ring to induce decomposition producing a singlet-excited carbonyl(s) effectively. Among them, a phosphate derivative (AMPPD® or PPD®)(**1c**) is now being used for biochemical and clinical applications.[9]

(Scheme1)



One outstanding structural characteristic of dioxetanes (**1a-c**) is that they possess an adamantylidene group as a stabilizer to maintain thermal persistency of the four-membered ring peroxide. An adamantylidene group has indeed been often used as a substituent for a variety of dioxetanes[1-3] after the discovery of bisadamantylidenedioxetane[10] which is the most stable thermally among dioxetanes hitherto known. However, an inevitable defect of the adamantylidene group is its lack of flexibility for structural modifications to design and develop new chemiluminescent substrates.

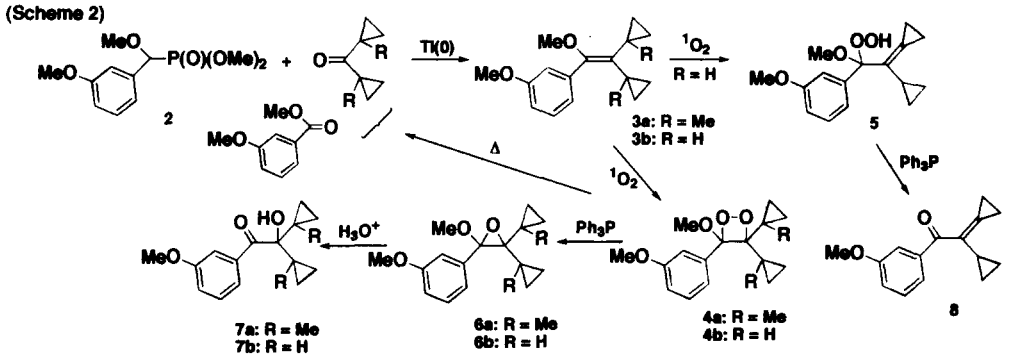
0040-4020/99/$ - see front matter
PII: S0040-4020(99)00124-6

These facts prompted us to synthesize 3-alkoxy-3-aryl-1,2-dioxetanes having two alkyl groups instead of an adamantylidene at the 4-position and to examine whether these dioxetanes are stable thermally as well and become a lead compound to develop further new chemiluminescent substrates. We describe here that an isopropyl group satisfies considerably these demands and disclose several other interesting results found out in the course of the investigation.[11-13]

Results and Discussion

[Singlet oxygenation of 1-alkoxy-2,2-dialkyl-1-(3-methoxyphenyl)ethylenes and thermal stability of 3-alkoxy-4,4-dialkyl-3-(3-methoxyphenyl)-1,2-dioxetanes] 1,2-Addition of singlet oxygen to olefins is a convenient process to synthesize 1,2-dioxetanes, though it is surpassed by competitive "ene" reaction affording an allylic hydroperoxide, when olefins possess allylic hydrogen(s).[14,15] On the other hand, sterically too congested olefins have been known to undergo singlet oxygenation sluggishly. Thus, first of all, we examined whether singlet oxygenation occurs or does not occur for an α-alkoxystyrene bearing only *tert*-alkyls to give effectively a dioxetane. Our choice of such olefin was a 1,1-bis(1-methylcyclopropyl)ethylene (**3a**), which was synthesized by Horner-Wittig reaction of a phosphate (**2**) with bis(1-methylcyclopropyl) ketone.[16]

(Scheme 2)

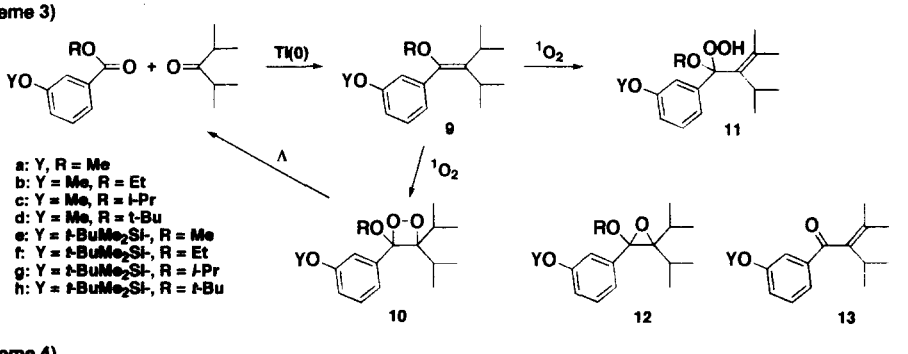


When an olefin (**3a**) was irradiated in the presence of tetraphenylporphin (TPP) with Na-lamp under an oxygen atmosphere at 0 °C, singlet oxygenation occurred smoothly to give a dioxetane (**4a**) as the sole product. The structure of **4a** was determined by ^{1}HNMR, ^{13}CNMR, IR, and Mass spectral analysis. A dioxetane (**4a**) decomposed to give exclusively methyl 3-methoxybenzoate and bis(1-methylcyclopropyl) ketone in hot toluene, while it was reduced with Ph_3P to afford an epoxide (**6a**), which was further hydrolyzed to a ketoalcohol (**7a**). To know thermal stability, the rates of decomposition of **4a** were measured at various temperatures by ^{1}HNMR, and their activation parameters were estimated from Arrhenius plots. The results clarified that **4a** is very stable thermally at 25 °C (half-life $t_{1/2}$ = 2.3 y). Next, a 1,1-dicyclopropylethylene (**3b**) was prepared similarly from **2** and dicyclopropyl ketone and its transformation to a dioxetane was attempted, though olefins bearing a cyclopropyl(s) have been reported to undergo "ene" reaction with singlet oxygen preferentially.[17] In fact, "ene" reaction took place at 0 °C to give an allylic hydroperoxide (**5**) as the main product, along with a dioxetane (**4b**) (**4b** : **5** = 32 : 68). The singlet oxygenation of **3b** at 25 °C afforded a 22 : 78 mixture of **4b** and **5**, while **4b** was formed predominantly (**4b** : **5** = 67 : 33), when the oxygenation was carried out at -78 °C. The results on mode selectivities between the 1,2-addition giving dioxetane and the "ene" reaction yielding hydroperoxide for **3b** at various temperatures are summarized together with those for **9** (*vide infra*) in **Table 1**.

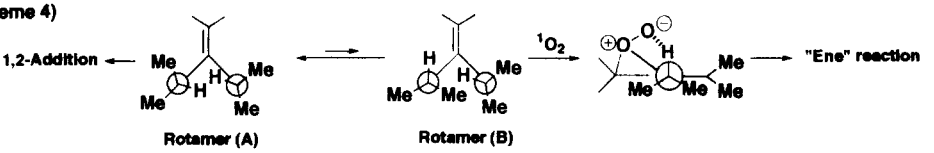
A hydroperoxide (**5**) was easily reduced with Ph_3P to give an unsaturated ketone (**8**). The kinetic experiment on thermal decomposition of **4b** yielding methyl *m*-methoxybenzoate and dicyclopropyl ketone was carried out as in the case of **4a**, and activation parameters *Ea* and log *A*, and half-lives $t_{1/2}$ at 25 °C for thermal decomposition of **4b** were estimated as shown in **Table 2**, where those of **4a** and **10** are also cited. These results reveal that **4b** is far more labile thermally than **4a**, and suggest that a steric interaction between *geminal* alkyls acts to stabilize the dioxetane skeleton for **4**, as reported for rather simple 3,3-dialkyl-1,2-dioxetanes,[18] and a cyclopropyl is likely too small to maintain thermal persistency of the dioxetane. Thus, we attempted to synthesize a dioxetane (**10a**) bearing two isopropyls which are bulkier to some extent than cyclopropyl.

Diisopropylethylenes (**9**) were synthesized by McMurry coupling[19,20] of 3-methoxybenzoates with diisopropyl ketone. The singlet oxygenation of an olefin (**9a**) at low temperature (-78 °C) afforded preferentially a dioxetane (**10a**) and a small amount of a hydroperoxide (**11a**) (**10a** : **11a** = 95 : 5), while the reaction at 25 °C gave a hydroperoxide (**11a**) as the main product (**10a** : **11a** = 29 : 71) (see **Table 1**). The structures of these peroxides (**10a**) and (**11a**) were determined similarly to the cases of **4** and **5**; photolysate of **9a** including **10a** and **11a** was reduced with Ph_3P to give an epoxide (**12a**) and an enone (**13a**). Thermal stability of a dioxetane (**10a**) increased again to a large extent as shown in **Table 2**.

(Scheme 3)



(Scheme 4)



The results described above for singlet oxygenation of **3b** and **9a** show that the reaction temperature has a significant effect on the mode selectivity for singlet oxygenation of the allylic olefins. On the other hand, it is well known for singlet oxygenation that a) the "ene" reaction requires lower activation energy than the 1,2-addition,[21] and b) the "ene" reaction occurs preferentially for olefins having an allylic hydrogen which sometimes lies perpendicular to the plane of the double bond.[14,15] These facts and the above results suggest that an isopropyl methine hydrogen(s) of **9a** and even a cyclopropyl methine hydrogen(s) of **3b** are far from being at a 90 ° dihedral angle with respect to a plane of the double bond at low temperature. It has been reported for molecules such as *N,N*-diisopropylamides and *N,N*-diisopropylthioamides that the interaction, the so-called "gear effect", between two ispropyl groups at *geminal* positions[22,23] makes some energy minima with respect to rotation of isopropyls, and methine protons of isopropyls are far from being perpendicular to the trigonal frame at low temperature. These explanation can be equally applied to the present olefins, although the two isopropyls or cyclopropyls are attached to carbon instead of nitrogen as illustrated in **Scheme 4**, where a rotamer (**A**) producing a dioxetane is probably more stable than (**B**) affording an "ene" reaction product.

Similar singlet oxygenation was carried out at various temperatures for olefins bearing an ethoxy (**9b**), an isopropoxy (**9c**), or a *tert*-butoxy group (**9d**) in the place of a methoxy of **9a**, and products ratios (mode selectivity) between the corresponding dioxetanes (**10**) and allylic hydroperoxides (**11**) were measured by ^{1}HNMR. The results summarized in **Table 1** reveal that the 1,2-addition of singlet oxygen occurs the more preferentially as an alkoxy group becomes bulkier for **9**, and it takes place exclusively even at 25 °C for a *tert*-butoxy analogue (**9d**), suggesting that the rotation of two "gears" of isopropyls is likely affected by the bulkiness of the *vicinal* alkoxy group. Thermal stabilities of dioxetanes (**10b** -**10d**) were also examined and the results are summarized in **Table 2**, which shows that **10c** is the most stable thermally at 25 °C among the diisopropyldioxetanes (**10a** -**10d**).

Table 1 Temperature effect on mode selectivity between 1,2-addition and "ene" reaction for singlet oxygenation of 1-alkoxy-2,2-dialkyl-1-(3-methoxyphenyl)ethylenes (3b) and (9) [a,b]

Ethylene		Reaction temperature		
		25 °C 1,2-Addition : "Ene" r.	0 °C 1,2-Addition : "Ene" r.	-78 °C 1,2-Addition : "Ene" r.
3b		22 : 78	32 : 68	67 : 33
9a	MeO	29 : 71	69 : 31	95 : 5
9b	EtO	80 : 20	91 : 9	99 : 1
9c	*i*-PrO	98 : 2	99 : 1	-100 : 0
9d	*t*-BuO	-100 : 0	-100 : 0	-100 : 0

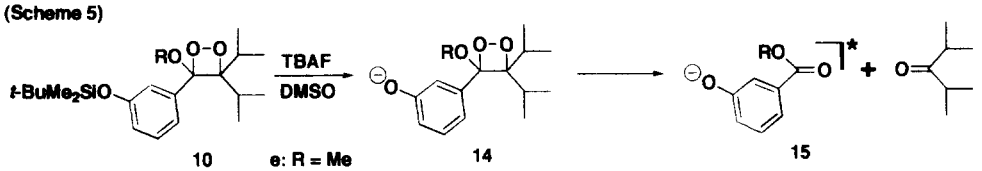
a) All the reactions were carried out in CH_2Cl_2. b) The ratios, 1,2-addition giving a 1,2-dioxetane *vs* "ene" reaction producing an allylic hydroperoxide, were measured by ^{1}HNMR of the corresponding photolysate of **3b** or **9**.

[Synthesis, thermal stability, and base-induced chemiluminescent decomposition of 3-alkoxy-3-(3-*tert*-butyldimethylsiloxyphenyl)-4,4-diisopropyl-1,2-dioxetanes] The results that the low-temperature singlet oxygenation of (methoxyphenyl)ethylenes (**9a** - **9d**) affords preferentially dioxetanes (**10a** - **10d**) encouraged us to synthesize dioxetanes (**10e** - **10h**) bearing a 3-(*tert*-butyldimethylsiloxy)phenyl group instead of a 3-methoxyphenyl. The singlet oxygenation of olefins (**9e** - **9h**) at -78 °C were easily attained to give **10e** - **10h**. The examination on thermal decomposition given in **Table 2** shows that all the diisopropyldioxetanes (**10**) are thermally stable enough to permit handling at room temperature, and their thermal stabilities are in the order of MeO < EtO < *i*-PrO >> *tert*-BuO for both series of methoxyphenyl (**10a** - **10d**) and siloxyphenyl derivatives (**10e** - **10h**). This order suggests that a steric interaction between *vicinal* substituents, a 3-alkoxy group and a 4-isopropyl, acts most likely to stabilize the dioxetane ring to some extent. However, it is notable that this type of steric interaction might rather act negatively when it becomes too large as in the case of *tert*-butoxy derivative (**10d** and **10h**), for which the steric interaction between a *tert*-butoxy and the *vicinal* isopropyl likely distorts the dioxetane ring and destabilizes it.

An adamantylidenedioxetane (**1b**) bearing a *m*-siloxyphenyl moiety has been reported to be easily triggered with tetrabutylammonium fluoride (TBAF) to generate an unstable dioxetane (**1d**) which decomposes rapidly to emit intense light (λmax = 466 - 470 nm) with high efficency (Φ_{CL} = 0.25 - 0.29 in DMSO).[8,24] Diisopropyldioxetanes (**10e** - **10h**) emitted also intense blue light (λmax = 463 nm) with Φ_{CL} and half-lives ($t_{1/2}$) as shown in **Table 2**, when solutions of dioxetanes (**10e** - **10h**) in DMSO (1.0 x 10^{-5} M, 1 mL) were added to TBAF solutions (1 x 10^{-2} M, 2 mL) at 25 °C. The results reveal that all these dioxetanes decompose to emit light as effectively as **1b**, though slower than **1b**. The emitter is the corresponding anion of benzoate (**15**) as in the case of **1b**, since fluorescence of **15** exhibits λmax equal essentially to the chemiluminescence of **10** in TBAF / DMSO. It should be noted here that half-life of the luminescence increases in the order of size of

the alkoxy group, that is MeO < EtO < *i*-PrO < *t*-BuO; **10h** has the longest half-life among **10e** - **10h** in spite of its much lower thermal stability compared to **10e** - **10g**.

(Scheme 5)



10 e: R = Me f: R = Et g: R = *i*-Pr h: R = *t*-Bu 14 15

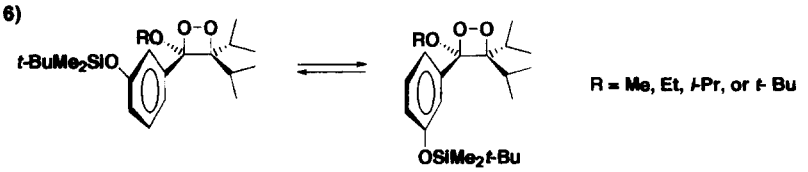
Table 2 Thermolysis and TBAF-induced chemiluminescent decomposition of 3-alkoxy-4,4-dialkyl-3 - aryl-1,2-dioxetanes (4) and (10).

Dioxetane	Thermolysis [a,b] *Ea* / kcal mol^{-1}	log *A*	$t_{1/2}$ at 25 °C / y [d]	Chemiluminescence [c] Φ_{CL} [e]	$t_{1/2}$ at 25 °C / s [f]
4a	29.7	13.7	2.3		
4b	22.5	10.7	0.012		
10a	27.8	12.6	1.3		
10b	27.9	12.6	1.5		
10c	28.2	12.6	2.3		
10d	28.3	13.0	1.2		
10e	25.5	11.3	0.53	0.21	6.3
10f	25.9	11.6	0.59	0.23	11.5
10g	26.7	11.9	0.91	0.35	20.5
10h	22.5	9.6	0.17	0.31	37.5

a) Thermolysis was carried out in benzene-d_6 or toluene-d_8 at 45 - 100 °C and first-order rates of decomposition were measured by ^{1}HNMR spectroscopy. b) Activation parameters reported partly in ref 13 are revised here. c) Solutions of **10e** - **10h** in DMSO (1.0 x 10^{-5} M, 1 mL) were added to TBAF solutions in DMSO (1.0 x 10^{-2} M, 2 mL) at 25 °C. d) Calculated values. e) Relative quantum yields based on the value for **1b**:[8] λ_{max} = 470 (463) nm, Φ_{CL} = 0.25, $t_{1/2}$ = 5 (4.7) s; values in parentheses were obtained in the present work. Φ_{CL} for **1b** has very recently been reported to be 0.29.[24]

The discrepancy in the order between thermal stabilities and half-lives of chemiluminescence for **10e** - **10h** is likely due to ease (rate) of the charge transfer from the phenoxide to the dioxetane ring in intermediary dioxetanes (**14e** - **14h**), considering that the order of thermal stabilities of **14** should reflect those of the parent dioxetanes **10**. On the other hand, an ^{1}HNMR study on the temperature dependency of signals due to the aromatic protons of **10** (-50 ~ 30 °C) showed the existence of energy barrier(s) **10h** >> **10e** - **10g** for the rotation of the aromatic ring in **10**; ^{1}HNMR spectral analysis showed that these dioxetanes (**10e** - **10g**) exist as 1 : 1 mixtures of two isomers at -50 °C, whereas **10h** exists as a 1 : 1 isomeric mixture even at 30 °C; plausible structures of these isomers are illustrated in **Scheme 6**. These facts suggest that the phenoxide ring in **14h** (RO = *t*-BuO) can not rotate freely to the conformation favorable for the intramolecular charge transfer from the phenoxide to the dioxetane ring.[25,26]

(Scheme 6)



Conclusion

Low-temperature singlet oxygenation was disclosed to be effective to synthesize 1,2-dioxetanes from 1-alkoxy-1-arylethylenes bearing *sec*-alkyls at the 2-position such as isopropyls (**9**) and cyclopropyls (**3**) though they possess allylic hydrogen(s) susceptible to "ene" reaction. The present work clarified that 3-alkoxy-3-aryl-4,4-diisopropyl-1,2-dioxetanes (**10e** - **10h**) are thermally persistent and decompose to emit light with efficiency as high as an adamantylidene derivative (**1b**) on treatment with TBAF in DMSO. These results suggest a promising possibility of designing dioxetanes as a new chemiluminescent substrate with alkyls or functionalized alkyls instead of an adamantylidene to satisfy various demands.

Experimental

Melting points were measured with a Yanako MP-S3 melting point apparatus and are uncorrected. IR spectra were taken on a JASCO FT/IR-300 fourier transform infrared spectrometer. ^{1}H and ^{13}CNMR spectra were recorded on JEOL EX-400 spectrometers. Deuteriochloroform (99.8 atom% enriched, Merck or Isotec) was used for the NMR solvent. ^{1}HNMR and ^{13}CNMR chemical shifts were reported in δ value based on internal TMS (δH = 0) or solvent signal ($CDCl_3$ δC = 77.0) as reference, and coupling constants (*J*) were reported by the use of Hz as a unit. Mass spectra were obtained by using JEOL JMS-SX-110A, JEOL JMS-AX-505H and/or Hitachi M80B mass spectrometers. Chemiluminescences were measured by Hitachi F-4010 spectrometer and/or Hamamatsu Photonics PMA-11 multi-channel detector. Reagents were purchased from Aldrich, Tokyo Chemical Industries, and/or Wako Pure Chemical Industries. Column chromatography was carried out with Wako gel C-200.

Synthesis of 1-alkoxy-2,2-dialkyl-1-arylethylenes (3) and (9): (3-Methoxyphenyl)ethylenes (**3a**, **3b**) were synthesized from dimethyl methoxy(3-methoxyphenyl)methanephosphonate and bis(1-methycyclopropyl) ketone[27] or dicyclopropyl ketone by a modification of reported method.[16] Olefins (**9a** - **9d**) and (3-*tert*-butyldimethylsiloxyphenyl)ethylene (**9e**) were synthesized by McMurry coupling[19,20] of the corresponding dialkylketones and *m*-methoxybenzoates. (3-*tert*-Butyldimethylsiloxyphenyl)ethylenes (**9f** - **9h**) were prepared from (3-methoxyphenyl)ethylenes (**9b** - **9d**) by demethylation with EtSNa in DMF and successive silylation with *tert*-butyldimethylsilyl chloride. As typical procedures, preparations of 1-methoxy-1-(3-methoxyphenyl)-2,2-bis(1-methylcyclopropyl)ethylene (**3a**), 1,1-diisopropyl-2-methoxy-2-(3-methoxyphenyl)ethylene (**9a**) and 1-(3-*tert*-butyldimethylsiloxyphenyl)-1-ethoxy-2,2-diisopropylethylene (**9f**) are described below.

1-Methoxy-1-(3-methoxyphenyl)-2,2-bis(1-methylcyclopropyl)ethylene (3a): Dimethyl methoxy-(3-methoxyphenyl)methanephosphonate (9.84 g, 37.8 mmol) was added to a solution of lithium diisopropylamide (47.4 mmol) in THF-hexane (50 mL) under N_2 atmosphere at -78 °C and then stirred at room temperature for 30 min. To the solution, bis(1-methylcyclopropyl) ketone (1.1 g, 8.0 mmol) was added and stirred for 1h. The mixture was poured into NaCl aq. solution and extracted with hexane. The organic layer was washed with NaCl aq. solution, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel and eluted with hexane to give **3a** as a colorless oil (600 mg, 28 %). ^{1}HNMR: 0.06 - 0.22 (m, 4H), 0.50 - 0.54 (m, 2H), 0.83 - 0.88 (m, 2H), 1.22 (s, 3H), 1.28 (s, 3H), 3.34 (s, 3H), 3.82 (s, 3H), 6.82 - 6.87 (m, 2H), 6.90 (d, *J* = 7.8, 1H), 7.25 (dd, *J* = 8.8 and 7.8, 1H). IR(liquid film): 3080, 2950, 2830, 1600, 1450 cm^{-1}; Mass (m/z, %): 272 (M^+, 11), 257 (16), 241 (100), 225 (87), 211 (21), 165 (93). HRMS m/z 272.1762, calcd for $C_{18}H_{24}O_2$ 272.1776.

After following the above procedure using dicyclopropyl ketone, 1,1-dicyclopropyl-2-methoxy-2(3-methoxyphenyl)ethylene (**3b**) was obtained as colorless crystals melted at 32.0 - 32.5 °C (74 % yield). ^{1}HNMR 0.02 - 0.15 (m, 2H), 0.35 - 0.47 (m, 2H), 0.66 - 0.79 (m, 4H), 1.10 - 1.19 (m, 1H), 1.75 - 1.83 (m, 1H), 3.38 (s, 3H), 3.81 (s, 3H), 6.83 (d with fine coupling, J = 8.3, 1H), 6.95 (s with fine coupling, 1H), 6.99 (d, J = 7.8, 1H), 7.24 (dd, J = 8.3 and 7.8, 1H). IR (KBr): 3100, 2950, 2800, 1600, 1460 cm^{-1}. Mass (m/z, %): 244 (M^+, 42), 213 (100), 203 (18), 171 (28), 137 (88), 121 (35).

1,1-Diisopropyl-2-methoxy-2-(3-methoxyphenyl)ethylene (9a): $LiAlH_4$ (1.14 g, 30 mmol) was added to a solution of titanium (III) trichloride (9.0 g, 58 mmol) in dry THF (100 mL) under Ar atmosphere at ice-cooled temperature. To the solution, triethylamine (4.2 mL, 30 mmol) was added at room temperature, and then stirred at refluxing temperature for 15 min. Under refluxing, a solution of methyl 3-methoxybenzoate (1.0 g, 6.0 mmol) and diisopropyl ketone (1.8 mL, 12.7 mmol) in dry THF (30 mL) was added dropwise for 20 min to the solution of low-valent titanium prepared above. After refluxing for 30 min, the reaction mixture was poured into ice water, and extracted with ethyl acetate. The organic layer was washed successively with water, aq. $NaHCO_3$, and saturated aq. NaCl, dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was chromatographed on silica gel and eluted with hexane-ethyl acetate (20 : 1) to give 630 mg of **9a** as a colorless oil (42.2 % yield). ^{1}HNMR: 0.92 (d, J = 6.8, 6H), 1.25 (d, J = 7.3, 6H), 2.32 (sept, J = 7.3, 1H), 2.46 (sept, J = 6.8, 1H), 3.19 (s, 3H), 3.81 (s, 3H), 6.79 - 6.85 (m, 3H), 7.24 (t, J = 7.8, 1H). IR (liquid film): 3070, 2950, 2870, 1600, 1480 cm^{-1}. Mass (m/z, %): 248 (M^+, 43), 205 (93), 233 (100), 57(77). HRMS 248.1790, calcd for $C_{16}H_{24}O_2$ 248.1776.

After following the above procedure using the corresponding combination of an ester, ethyl, isopropyl, *tert*-butyl ester of 3-methoxybenzoate, or methyl 3-(*tert*-butyldimethylsiloxy)benzoate, ethylenes (**9b** - **9e**) were obtained as a colorless oil; **9b**: 60 %, **9c**: 67 %, **9d**: 47 %, and **9e**: 52 %.

9b: ^{1}HNMR: 0.92 (d, J = 6.8, 6H), 1.17(t, J = 7.1, 3H), 1.26 (d, J = 6.8, 6H), 2.33 (sept, J = 6.8, 1H), 2.45 (sept, J = 6.8, 1H), 3.33 (q, J = 7.1, 2H), 3.81 (s, 3H), 6.78 - 6.87 (m, 3H), 7.22 - 7.27 (m, 1H). IR (liquid film): 2960, 2870, 1600, 1465, 1360 cm^{-1}. Mass (m/z, %): 262 (M^+, 13), 247 (32), 219 (15), 135 (53), 107 (23), 92 (48), 55 (100).

9c: ^{1}HNMR: 0.89 (d, J = 6.8, 6H), 1.09 (d, J = 6.4, 6H), 1.26 (d, J = 6.8, 6H), 2.41 (sept, J = 6.8, 2H), 3.64 (sept, J = 6.4, 1H), 3.81 (s, 3H), 6.78 (s with fine coupling, 1H), 6.80 - 6.85 (m, 2H), 7.21 - 7.27 (m, 1H). IR (liquid film): 3080, 2870, 1568, 1381, 1369. Mass (m/z, %): 276 (M^+, 23), 234 (24), 219 (71),199 (18), 191 (100), 156 (37), 135 (39).

9d: ^{1}HNMR: 0.88 (d, J = 6.8, 6H), 1.08 (s, 9H), 1.24 (d, J = 7.1, 6H), 2.40 (sept, J = 6.8, 1H), 2.64 (sept, J = 7.1, 1H), 3.81 (s, 3H), 6.81 (d with fine coupling, J = 7.8, 1H), 6.84 (s with fine coupling, 1H), 6.88 (d, J = 7.8, 1H), 7.20 (t, J = 7.8, 1H). IR (liquid film): 3080, 2870, 1620, 1600, 1364 cm^{-1}. Mass (m/z, %): 290 (M^+, 4), 234 (47), 219 (43),191 (100), 135 (40).

9e: ^{1}HNMR: 0.19 (s, 6H), 0.91 (d, J = 6.8, 6H), 0.99 (s, 9H), 1.24 (d, J = 6.8, 6H), 2.31 (sept, J = 6.8, 1H), 2.45 (sept, J = 6.8, 1H), 3.18 (s, 3H), 6.73 (s with fine coupling, 1H), 6.78 (d with fine coupling, J = 8.1, 1H), 6.85 (d with fine coupling, J = 7.5, 1H), 7.19 (dd, J = 8.1, 7.5, 1H). IR (liquid film): 2955, 2830, 1600, 1480, 1285 cm^{-1}. Mass (m/z, %): 348 (M^+, 36), 333 (100), 306(74), 290 (48), 217 (43).

1-(3-*tert*-Butyldimethylsiloxyphenyl)-1-ethoxy-2,2-diisopropylethylene (9f): A solution of 1-ethoxy-2,2-diisopropyl-1-(3-methoxyphenyl)ethylene (**9b**) (300 mg, 1.14 mmol) and EtSNa (2.03 mmol, prepared from EtSH and NaH *in situ*) in DMF (6 mL) was refluxed under N_2 for 3 h. After cooling, the mixture was poured into sat. NaCl solution, extracted with AcOEt, dried over $MgSO_4$, and concentrated *in*

vacuo. The residue was chromatographed on silica gel and eluted with hexane-AcOEt (5 : 1) to give 1-ethoxy-2,2-diisopropyl-1-(3-hydroxyphenyl)ethylene as a colorless oil (250 mg, 88 %): ^{1}HNMR: 0.91 (d, J = 6.8, 6H), 1.16(t, J = 7.1, 3H), 1.25 (d, J = 6.8, 6H), 2.34 (sept, J = 6.8, 1H), 2.45 (sept, J = 6.8, 1H), 3.33 (q, J = 7.1, 2H), 5.29 (br s, 1H), 6.74 - 6.81 (m, 2H), 6.82 (d, J = 7.3, 1H), 7.19 (dd, J = 7.8, 7.3, 1H) ppm; IR (liquid film): 3400, 2975, 2870, 1590, 1360, 1280, 1225, 1115, and 1070 cm^{-1}; Mass (m/z, %): 248 (M^+, 32), 218 (84), 191 (100), and 135 (53). *tert*-Butyldimethylsilyl chloride (300 mg, 1.99 mmol) and K_2CO_3 (0.3 g, 2.17 mmol) were added to a solution of 1-ethoxy-1-(3-hydroxyphenyl)-2,2-diisopropylethylene (200 mg, 0.81 mmol) in dry DMF (5 mL) at ice-cooled temperature and then stirred at room temperature overnight. The solution was washed with water and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel and eluted with hexane-AcOEt (10 : 1) to afford the title compound as a colorless oil (156 mg, 54 %). **9f:** ^{1}HNMR: 0.19 (s, 6H), 0.91 (d, J = 6.8, 6H), 0.98 (s, 9H), 1.16(t, J = 7.0, 3H), 1.25 (d, J = 6.8, 6H), 2.32 (sept, J = 6.8, 1H), 2.44 (sept, J = 6.8, 1H), 3.32 (q, J = 7.0, 2H), 6.73 (s with fine coupling, 1H), 6.77 (ddd, J = 8.3, 2.4, 1.0, 1H), 6.85 (d with fine coupling, J = 7.3, 1H), 7.18 (dd, J = 8.3 and 7.3, 1H). IR (liquid film): 2960, 2870, 1600, 1480, 1285 cm^{-1}. Mass (m/z, %): 362 (M^+, 76), 348 (28), 347(100), 319 (61), 235 (13). HRMS 362.2656, calcd for $C_{22}H_{38}O_2Si$ 362.2641.

After following the above procedure using **9c** or **9d**, ethylenes (**9g** and **9h**) were obtained; **9g:** 85.2 % (based on **9c**) as a colorless oil, **9h:** 60.6 % (based on **9d**) as a colorless oil.

9g: ^{1}HNMR: 0.19 (s, 6H), 0.88 (d, J = 6.8, 6H), 0.98 (s, 9H), 1.08 (d, J = 6.4, 6H), 1.25 (d, J = 6.8, 6H), 2.40 (sept, J = 6.8, 2H), 3.63 (sept, J = 6.4, 1H), 6.72 (s with fine coupling, 1H), 6.77 (ddd, J = 8.3, 2.4, 1.0, 1H), 6.84 (d with fine coupling, J = 7.3, 1H), 7.18 (dd, J = 8.3, 7.3, 1H). IR (liquid film): 2960, 2860, 1600, 1465, 1270 cm^{-1}. Mass (m/z, %): 376 (M^+, 30), 333 (12), 318 (35), 290(56), 234 (49), 163 (10), 73 (100).

9h: ^{1}HNMR: 0.17 (s, 6H), 0.87 (d, J = 6.8, 6H), 0.98 (s, 9H), 1.08 (s, 9H), 1.24 (d, J = 7.0, 6H), 2.38 (sept, J = 7.0, 1H), 2.63 (sept, J = 6.8, 1H), 6.72 - 6.79 (m, 2H), 6.89 (d with fine coupling, J = 7.3, 1H), 7.14 (dd, J = 8.3, 7.3, 1H). IR (liquid film): 2960, 1600, 1480, 1260, 1175 cm^{-1}. Mass (m/z, %): 390 (M^+, 4), 333 (100), 318(44), 290 (82), 234 (9).

Singlet Oxygenation of 1-Alkoxy-2,2-dialkyl-1-arylethylenes: A solution of an ethylene (**3**) or (**9**) (50 - 100 mg) and TPP (5 mg) in CH_2Cl_2 (10 mL) was irradiated externally with 940 W Na lamp under an oxygen atmosphere for 1 - 2 h. The photolysate was concentrated *in vacuo* at < room temperature and analyzed by ^{1}HNMR ($CDCl_3$).

For isolation of 1,2-dioxetanes (**4**) and (**10**), the singlet oxygenation was carried out at -78 °C. The photolysate was chromatographed on silica gel and eluted with hexane / AcOEt (20 : 1) to give a dioxetane. All dioxetanes (**4**) and (**10**) except for **4a** and **10a** were obtained as a pale yellow oil and their spectral data are shown below. Isolated yields were 90 % for **4a** (pale yellow plates melted at 35.5 - 37.0 °C), 53 % for **4b**, 80 % for **10a** (pale yellow granules melted at 36.0 - 37.0 °C), 82 % for **10b**, 54 % for **10c**, 71 % for **10d**, 76 % for **10e**, 83 % for **10f**, 88 % for **10g**, and 69 % for **10h**.

4a: ^{1}HNMR: -0.07 - -0.02 (m, 1H), 0.12 - 0.18 (m, 1H), 0.24 - 0.30 (m, 1H), 0.38 - 0.44 (m, 1H), 0.47 - 0.58 (m, 2H), 0.70 (s, 3H), 1.35 - 1.43 (m, 2H), 1.38 (s, 3H), 3.12 (s, 3H), 3.85 (s, 3H), 6.93 (d with fine coupling, J = 8.3, 1H), 7.19 (d, J = 7.8, 1H), 7.20 (broad s, 1H), 7.33 (dd, J = 8.3, 7.8, 1H). ^{13}CNMR: 8.4, 9.9, 13.3, 13.5, 19.3, 19.7, 21.9, 23.9, 49.4, 55.3, 94.4, 113.2, 114.4, 114.6, 120.9, 128.9, 137.4, 159.4.

IR (KBr): 3100, 3000, 2830, 1600, 1460,1285, 1170, 1075 cm^{-1}. Mass (m/z, %): 272 (M^+-O_2, trace), 166 (97), 135 (100), 123 (15). HRMS M^+-O_2 272.1771, calcd for $C_{18}H_{24}O_2$ 272.1776. CIMS MH^+ 305.

4b: ^{1}HNMR: 0.03 - 0.11 (m, 1H), 0.20 - 0.43 (m, 4H), 0.56 - 0.70 (m, 2H), 0.80 - 0.92 (m, 2H), 1.76 - 1.84 (m, 1H), 3.15 (s, 3H), 3.84 (s, 3H), 6.90 (d with fine coupling, J = 8.3, 1H), 7.01 (broad s, 1H), 7.02 (d, *J* = 7.8, 1H), 7.32 (dd, *J* = 8.3, 7.8, 1H). ^{13}CNMR: 1.4, 1.6, 1.6, 1.7, 11.9, 12.6, 50.0, 55.3, 93.0, 112.5, 113.0, 114.3, 119.3, 129.2, 137.7, 159.5. IR (liquid film): 3100, 2950, 2800, 1600, 1460,1285, 1030 cm^{-1}. Mass (m/z, %): 244 (M^+- O_2, trace), 166 (83), 135 (100), 107 (30). HRMS M^+-O_2 244.1457, calcd for $C_{16}H_{20}O_2$ 244.1463. CIMS MH^+ 277.

10a: ^{1}HNMR: 0.46 (d, *J* = 6.8, 3H), 0.92 (d, *J* = 6.8, 3H), 1.18 (d, *J* = 7.3, 3H),1.30 (d, *J* = 7.3, 3H), 2.46 (sept, *J* = 7.3, 1H), 2.59 (sept, *J* = 6.8, 1H), 3.14 (s, 3H), 3.84 (s, 3H), 6.80 - 7.40 (m, 3H), 6.93 (d with fine coupling, J = 8.3, 1H). ^{13}CNMR: 16.6, 17.2, 18.5, 19.4, 29.2, 33.5, 49.4, 55.4, 98.2, 114.4, 114.6, 115 (br), 120 (br), 129.3, 137.0, 159.6. IR (KBr): 3100, 2950, 2800, 1600, 1460, 1285, 1030 cm^{-1}. Mass (m/z, %): 248 (M^+- O_2, 53), 233 (37), 205 (37), 166 (71), 135 (100), 107 (31). HRMS M^+-O_2 248.1787, calcd for $C_{16}H_{24}O_2$ 248.1776. CIMS MH^+ 281.

10b: ^{1}HNMR: 0.45 (d, *J* = 7.3, 3H), 0.90 (d, *J* = 6.8, 3H), 1.21 (d, *J* = 7.3, 3H), 1.26 (t, *J* = 7.1, 3H), 1.34 (d, *J* = 6.8, 3H), 2.41 (sept, *J* = 7.3, 1H), 2.56 (sept, *J* = 6.8, 1H), 3.10 (dq, *J* = 9.3, 7.1, 1H), 3.54 (dq, *J* = 9.3, 7.1, 1H), 3.84 (s, 3H), 6.91 (d with fine coupling, *J* = 8.3, 1H), 6.88 - 7.38 (m, 3H). ^{13}CNMR: 15.3, 16.3, 17.2, 18.7, 19.4, 29.0, 33.4, 55.3, 57.8, 98.2, 114.0, 114.5, 115 (br), 120 (br), 129.2, 137.8, 159.5. IR (liquid film): 2975, 1600, 1465, 1290, 1110, 1040 cm^{-1}. Mass (m/z, %): 262 (M^+- O_2, 13), 247(10), 180(70), 152 (24), 135 (100). HRMS M^+-O_2 262.1913, calcd for $C_{17}H_{26}O_2$ 262.1933. CIMS MH^+ 295.

10c: ^{1}HNMR: 0.47 (d, *J* = 7.3, 3H), 0.87 (d, *J* = 6.8, 3H), 1.10 (d, *J* = 6.1, 3H), 1.21 (d, *J* = 7.3, 3H), 1.30 (d, *J* = 6.1, 3H), 1.36 (d, *J* = 7.3, 3H), 2.41 (sept, J = 7.3, 1H), 2.46 (sept, J = 6.8, 1H), 3.58 (sept, *J* =5.9, 1H), 3.84 (br s, 3H), 6.86 - 7.46 (m, 4H). ^{13}CNMR: 16.3, 17.3, 18.8, 19.4, 23.6, 24.7, 29.1, 33.4, 55.3, 67.7, 98.5, 113.0, 114.5, 120.0, 121.5, 128.9, 138.6, 159.3. IR (liquid film): 3090, 2971, 2936, 2879, 1600, 1100 cm^{-1}. Mass (m/z, %): 276 (M^+- O_2), 234 (9), 194 (68),152 (79), 135 (100), 114 (22), 107 (21). HRMS M^+-O_2 276.2082, calcd for $C_{18}H_{28}O_2$ 276.2089. CIMS MH^+ 309.

10d (1 : 1 isomeric mixture): ^{1}HNMR: 0.39 (d, *J* = 6.8, 3H), 0.88 (d, *J* = 6.8 Hz, 3H), 1.19 (s, 12H), 1.33 (d, *J* = 6.8, 3H), 2.44 (sept, *J* = 6.8, 1H), 3.80 and 3.85 (two s, 3H), 6.85 - 7.38 (m, 4H). ^{13}CNMR: 16.5, 17.2, 18.7, 19.4, 29.5, 31.0, 31.0, 33.1, 33.2, 55.3, 78.3, 99.1, 113.5, 113.7, 113.9, 114.2, 120.6, 128.4, 128.9, 142.5, 158.9, 159.3. IR (liquid film): 3080, 2973, 2879, 2836, 1602,1100 cm^{-1}. Mass (m/z, %): 290 (M^+-O_2, 1), 208 (26), 191 (32), 152(100), 135 (54), 107 (11). HRMS M^+-O_2 290.2234, calcd for $C_{19}H_{30}O_2$ 290.2246. CIMS MH^+ 323.

10e: ^{1}HNMR: 0.20 (s, 6H), 0.46 (d, *J* = 7.3, 3H), 0.92 (d, *J* = 6.8, 3H), 0.99 (s,9H), 1.17 (d, *J* = 7.3, 3H), 1.30 (d, *J* = 6.8, 3H), 2.46 (sept, *J* = 7.3, 1H), 2.60 (sept, *J* = 6.8, 1H), 3.13 (s, 3H), 6.87 (d with fine coupling, *J* = 9.0, 1H), 6.80 - 7.40 (m, 3H). ^{13}CNMR: -4.4, 16.6, 17.2, 18.3, 18.4, 19.3, 25.7, 29.2, 33.4, 49.4, 98.3, 114.4, 121(br), 129.3, 137.0, 155.8. IR (liquid film): 2960, 2860, 1600, 1480, 1430,1290, 1115, 1010 cm^{-1}. Mass (m/z, %): 348 (M^+- O_2, 6), 266 (20), 235 (12), 210 (21), 209 (100). HRMS M^+-O_2 348.2493, calcd for $C_{21}H_{36}O_2Si$ 348.2484. CIMS MH^+ 381.

10f: ^{1}HNMR: 0.19 (s, 6H), 0.44 (d, *J* = 6.8, 3H), 0.91 (d, *J* = 6.8, 3H), 0.99 (s, 9H), 1.20 (d, J = 6.8, 3H), 1.27 (t, *J* = 6.8, 3H), 1.33 (d, *J* = 6.8, 3H), 2.40 (sept, *J* = 6.8, 1H), 2.58 (sept, *J* = 6.8, 1H), 3.10 (dq, *J* = 9.3, 6.8, 1H), 3.55 (dq, *J* = 9.3, 6.8, 1H), 6.86 (d with fine coupling, *J* = 8.3, 1H), 6.84 - 7.31 (m, 3H).

^{13}CNMR: -4.4, 15.3, 16.4, 17.1, 18.2, 18.7, 19.4, 25.7, 29.0, 33.4, 57.7, 98.2, 113.9, 121 (br), 129.2, 137.7, 155.7. IR (liquid film): 2960, 1600, 1480, 1290, 1110 cm^{-1}. Mass (m/z, %): 362 (M^+-O_2 , 5), 280 (24), 235 (12), 224 (24), 223 (100), 195 (13). HRMS M^+-O_2 362.2660, calcd for $C_{22}H_{38}O_2Si$ 362.2641. CIMS MH^+ 395.

10g: ^{1}HNMR: 0.20 (br s, 6H), 0.47 (br d, J = 6.8, 3H), 0.87 (d, J = 6.8, 3H), 0.99 (s, 9H), 1.10 (br d, J = 5.9, 3H), 1.20 (d, J = 6.8, 3H), 1.30 (d, J = 5.9, 3H), 1.35 (d, J = 6.8, 3H), 2.40 (sept, J = 6.8, 1H), 2.48 (sept,J = 6.8, 1H), 3.60 (sept, J = 5.9, 1H), 6.80 - 7.40 (m, 4H). ^{13}CNMR: -4.4, 16.4, 17.3, 18.2, 19.4, 23.7, 24.7, 25.7, 29.1, 33.3, 67.7, 98.6, 114.4, 118.7, 120.7, 121.2, 122.2, 128.8, 138.6, 155.5. IR (liquid film): 2960, 1600, 1465, 1270, 1100 cm^{-1}. Mass (m/z, %): 376 (M^+-O_2 , 5), 294 (19), 237 (29), 235 (13), 195 (100). HRMS M^+-O_2 376.2771, calcd for $C_{23}H_{40}O_2Si$ 376.2797. CIMS MH^+ 409.

10h (1 : 1 isomeric mixture): ^{1}HNMR: 0.17 and 0.18 (two s, 3H), 0.19 (s, 3H), 0.36 and 0.38 (two d, J = 6.8, 3H), 0.89 (d, J = 6.8, 3H), 0.98 and 0.99 (two s, 9H), 1.17 and 1.18 (two d, J = 6.8, 3H), 1.19 and 1.21 (two s, 9H), 1.32 (d, J = 6.8, 3H), 2.40 and 2.41 (two sept, J = 6.8, 1H), 2.57 and 2.61 (two sept, J = 6.8, 1H), 6.82 (d with fine coupling, J = 7.8, 1H), 6.93 (s with fine coupling, 0.5H), 7.06 (d with fine coupling, J = 7.8, 0.5H), 7.18 and 7.24 (two t, J = 7.8, 1H), 7.24 (s with fine coupling, 0.5H), 7.34 (d with fine couping, J = 7.8, 0.5H). ^{13}CNMR: -4.4, -4.3, -4.2, 16.5, 17.1, 17.2, 18.2, 18.3, 18.7, 19.4, 25.7, 25.8, 29.2, 29.3, 30.9, 33.0, 33.2, 78.2, 99.0, 113.5, 113.7, 119.2, 120.2, 120.4, 120.7, 121.1, 121.3, 128.4, 128.9, 142.5, 155,1, 155.4. IR (liquid film): 2965, 2860, 1600, 1480, 1365,1290, 1110 cm^{-1}. Mass (m/z, %): 390 (M^+-O_2, trace), 294 (14), 237 (20), 235 (12), 223 (16), 195 (100). HRMS M^+-O_2 390.2941, calcd for $C_{24}H_{42}O_2Si$ 390.2954. CIMS MH^+ 423.

For isolation of hydroperoxides (5) and (11a), the singlet oxygenation was carried out at 25 °C and the photolysate was similarly chromatographed on silica gel. The isolation was successful only for **5**, which was obtained as a colorless oil in 60 % yield and its spectral data are given below. A hydroperoxide (**11a**) was unstable and decomposed during isolation process by chromatography to give a complex mixture including an unsaturated ketone (**13**) (*vide infra*). The product ratios (**10** : **11**) were tentatively measured by comparing ^{1}HNMR spectrum of a photolysate of **9** with the corresponding spectrum of **10**, and the results are summarized in **Table 1**.

2-Cyclopropyl-2-cyclopropylidene-1-hydroperoxy-1-methoxy-1-(3-methoxyphenyl)ethane (5): ^{1}HNMR: 0.42 - 0.49 (m, 2H), 0.54 - 0.62 (m, 2H), 1.04 - 1.18 (m, 4H), 1.25 - 1.37 (m, 2H), 3.39 (s, 3H), 3.81 (s, 3H), 6.83 - 6.85 (m, 1H), 7.11 - 7.13 (m, 2H), 7.24 - 7.28 (m, 1H), and 7.48 (br s, 1H) ppm. IR (liquid film): 3400, 3005, 2940, 2835, 1600, 1490, 1270, 1080, 1050 cm^{-1}. Mass (m/z, %) 276 (M^+, 5), 259 (9), 243 (60), 228 (12), 213 (11), 199(23), 185 (12), 166 (39), 159 (10), 135 (100).

Reduction of 3-methoxy-3-(3-methoxyphenyl)-4,4-bis(1-methylcyclopropyl)-1,2-dioxetane (4a) as a typical procedure: A solution of a dioxetane (**4a**) (50 mg, 0.16 mmol) and triphenylphosphine (50 mg, 0.19 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 14 h. After concentration, the mixture was chromatographed on silica gel and eluted with hexane-AcOEt (20 : 1) to give 1-methoxy-1-(3-methoxyphenyl)-2,2-bis(1-methylcyclopropyl)-1,2-epoxyethane (**6a**) as a colorless oil in 69 % yield. ^{1}HNMR: -0.21 – -0.15 (m, 1H), 0.15 – 0.28 (m, 2H), 0.38 – 0.42 (m, 1H), 0.55 – 0.63 (m, 2H), 0.76 - 0.86 (m, 2H), 0.82 (s, 3H), 1.36 (s, 3H), 3.16 (s, 3H), 3.83 (s, 3H), 6.88 (d with fine coupling, J = 8.3, 1H), 7.06 (s with fine coupling, 1H), 7.12 (d with fine coupling, J = 7.8, 2H), 7.29 (dd, J = 8.3, 7.8, 1H). IR (liquid film): 3100, 2970, 2840, 1600, 1260, 1080 cm^{-1}. Mass (m/z, %) 288 (M^+, 1), 163 (37), 121 (34), 107 (100).

Hydrolysis of 1-methoxy-1-(3-methoxyphenyl)-2,2-bis(1-methylcyclopropyl)-1,2-epoxyethane (6a): A solution of an epoxide (**6a**) (20 mg) and *p*-toluenesulfonic acid hydrate (20 mg) in THF (1 mL) was stirred overnight at room temperature. After concentration, the mixture was chromatographed on silica gel and eluted with hexane-AcOEt (10 : 1) to give 2-hydroxy-1-(3-methoxyphenyl)-2,2-bis(1-methylcyclopropyl)ethanone (**7a**) as an oil in 68 % yield: ^{1}HNMR: 0.32 (m, 4H), 0.83 (d, J = 9.8, 2H), 0.91 (d, J = 9.8, 2H), 1.25 (s, 6H), 2.39 (br s, 1H), 3.83 (s, 3H), 7.02 (d with fine coupling, J = 8.3, 1H), 7.30 (dd, J = 8.3, 7.8, 1H), 7.37 (br s, 1H), 7.47 (d, J = 7.8, 1H). IR (liquid film): 3510, 3060, 1680, 1580, 1260, 1030 cm^{-1}. Mass (m/z, %) 274 (M^+, 1), 139 (100).

Reduction of 1-cyclopropyl-1-cyclopropylidene-2-hydroperoxy-2-methoxy-2-(3-methoxyphenyl)ethane (5): A solution of a hydroperoxide (**5**) (100 mg, 0.36 mmol) and triphenylphosphine (100 mg, 0.38 mmol) in CH_2Cl_2 (4 mL) was stirred at ice-cooled temperature for 1 h. After concentration, the mixture was chromatographed on silica gel and eluted with hexane-AcOEt (20 : 1) to give 2-cyclopropyl-2-cyclopropylidene-1-(3-methoxyphenyl)ethanone (**8**) as a colorless oil in 64 % (53 mg) yield. ^{1}HNMR: 0.76 - 0.98 (m, 6H), 1.19 - 1.39 (m, 2H), 2.00 (m, 1H), 3.83 (s, 3H), 6.95 - 7.39 (m, 4H). IR (liquid film): 3080, 3000, 2815, 1650, 1580 cm^{-1}. Mass (m/z, %) 228 (M^+, 32), 213 (16), 197 (20), 135 (100), 121 (20).

Reduction of photolysate of 2,2-diisopropyl-1-methoxy-1-(3-methoxyphenyl)ethylene (9a) as a typical procedure: A solution of a photolysate comprising of (**11a**) and (**10a**) (ca 7 : 3) (100 mg) and triphenylphosphine (100 mg, 0.38 mmol) in CH_2Cl_2 (4 mL) was stirred at ice-cooled temperature for 1 h. After concentration, the mixture was analyzed by ^{1}HNMR to show that it included 2-isopropyl-2-isopropylidene-1-(3-methoxyphenyl)ethanone (**13a**) and 1,1-diisopropyl-2-methoxy-2-(3-methoxyphenyl)-1,2-epoxyethane (**12a**) with a ratio similar to that of the starting mixture of peroxides. The mixture was chromatographed on silica gel and eluted with hexane-AcOEt (20 : 1) to give **13a** (colorless oil, 25 mg) and **12a** (colorless oil, 16 mg). **12a**: ^{1}HNMR: 0.75 (d, J = 6.8, 3H), 0.88 (d, J = 6.8, 3H), 1.02 (d, J = 6.8, 3H), 1.22 (d, J = 6.8, 3H), 2.34 (sept, J = 6.8, 1H), 3.13 (s, 3H), 3.83 (s, 3H), 6.87 (dd, J = 8.3, 2.4, 1H), 7.00 (br s, 1H), 7.06 (br d, J = 7.8, 1H), 7.28 (dd, J = 8.3, 7.8, 1H). IR (liquid film): 3050, 2960, 1600, 1265, 1215, 1115, 1050 cm^{-1}. Mass (m/z, %) 264 (M^+, 2), 221 (10), 166 (26), 135 (100). **13a**: ^{1}HNMR: 1.03 (d, J = 7.0, 6H), 1.51 (s, 3H), 1.83 (s, 3H), 2.95 (sept, J = 7.0, 1H), 3.86 (s, 3H), 7.02 - 7.15 (m, 1H), 7.35 (t, J = 7.9, 1H), 7.45 - 7.57 (m, 2H). IR (liquid film): 3075, 2960, 1660, 1595, 1040 cm^{-1}. Mass (m/z, %): 232 (M^+, 37), 217 (10), 201 (18), 189 (38), 135 (100).

Thermal decomposition of 3-alkoxy-4,4-dialkyl-3-aryl-1,2-dioxetanes; general procedure: A 0.01 - 0.02 M solution of a dioxetane in benzene-d_6 or toluene-d_8 was heated at various temperatures (45 - 100 °C) on thermostated bath and the time-course of decomposition of a dioxetane was monitored by ^{1}HNMR at regular time intervals (3 - 9 h) during max. 40 h. All the dioxetanes (**4**) and (**10**) were selectively decomposed into the corresponding benzoate and dialkyl ketone by a first-order process. The rates of decomposition and their thermodynamic parameters were calculated from Arrhenius plots.

The temperature dependency of ^{1}HNMR spectra of 3-alkoxy-3-(*tert*-butyldimethylsiloxyphenyl)-4,4-diisopropyl-1,2-dioxetanes: ^{1}HNMR spectra of **10e** -**10g** were measured in $CDCl_3$ at 30, 0, -30, and -50 °C. ^{1}HNMR spectral data cited above shows that only **10h** exists as a 1 : 1 mixture of two isomers among dioxetanes (**10e** - **10h**) even at 30 °C. On the other hand, ^{1}HNMR ($CDCl_3$) spectra of **10e** -**10g** exhibited that they exist as 1 : 1 mixtures at -30 ~ -50 °C. As a representative, chemical shifts of peaks due to aromatic protons of **10g** at -50 °C were as follows: 6.85 (s, 0.5H), 6.88 (d, J = 8.4, 0.5H), 6.90 (d, J = 7.8, 0.5H), 7.02 (d, J = 7.6, 0.5H), 7.26 (s, 0.5H), 7.22 - 7.35 (m, 1H), 7.37 (d, J = 7.2, 0.5H).

Chemiluminescence measurement of 3-alkoxy-3-(3-*tert*-butyldimethylsiloxyphenyl)-4,4-diisopropyl-1,2-dioxetanes; general procedure: From a freshly prepared solution of 1.0 x 10^{-2} M TBAF in DMSO was transferred 2 mL into a quartz cell (10 x 10 x 50 mm) and the latter placed into the spectrometer, which was thermostated at 25 °C. After ca. 3 min, a solution of the dioxetane in DMSO (1.0 x 10^{-5} M, 1 mL) was added by means of a syringe with immediate starting of measurement. The intensity of light emission - time-courses was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing with that of an adamantylidene dioxetane (**1b**) as a standard.[8]

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