THERMAL AND CHEMILUMINESCENT PROPERTY OF DIOXETANES HAVING AN *N*-ARYLACRIDANE STRUCTURE¶

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Abstract – Novel dioxetanes having an *N*-arylacridane structure were synthesized. Studies on thermal stability and chemiluminescent property of these compounds showed that the aryl group cannot stabilize the dioxetane structure so much but can trigger the chemiluminescence by formation of the phenoxy anion.

Dioxetanes are interesting compounds because of their potent chemiluminescent activity, especially stabilized ones triggered by some chemical or enzymatic treatment are anticipated to be a useful probe for highly sensitive detection of biomacromolecules.[1] Although some dioxetanes are used for such a purpose at present, there still remain problems in sensitivity, applicability, and/or stability.[2] Therefore, novel stabilized dioxetanes with potentially higher chemiluminescent activity are strongly demanded.

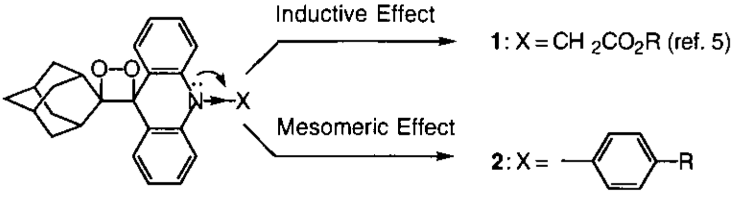
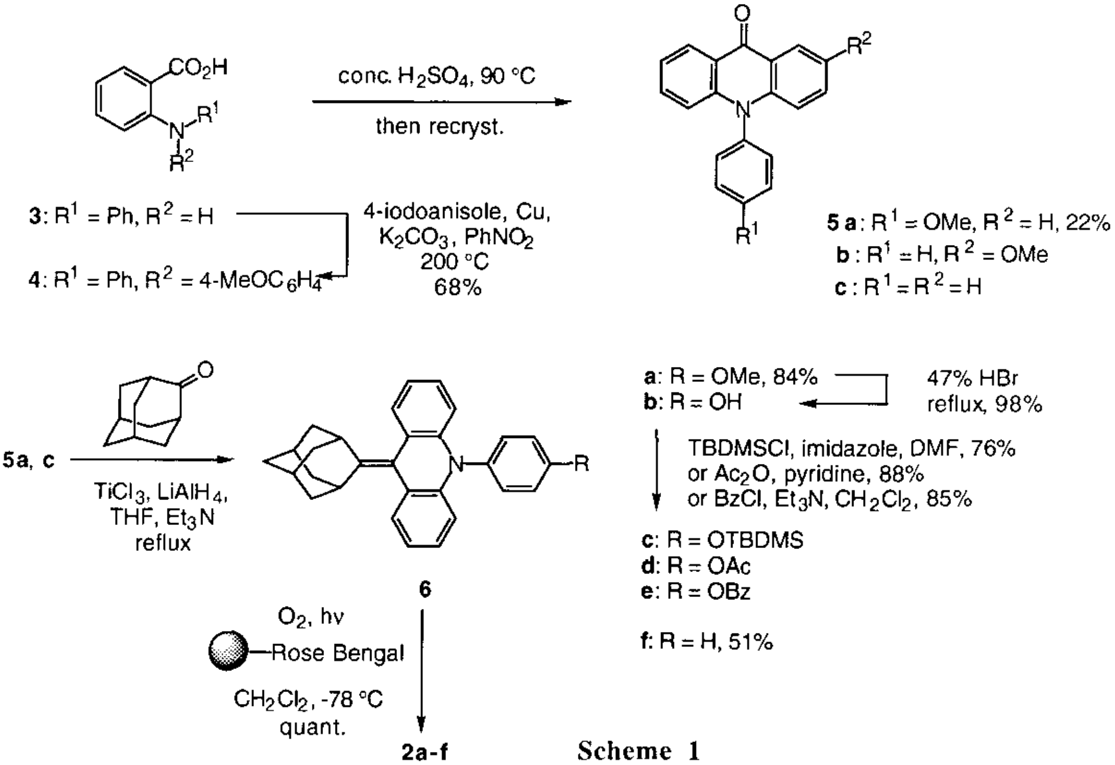


Figure 1

Upon designing novel dioxetanes, we combined a dioxetane structure with an acridane structure as a luminophore and an adamantane structure which is known to stabilize the dioxetane structure sterically as shown in Figure 1.[3] To stabilize the dioxetane structure more, we planned to introduce an electron-withdrawing group (X) on the nitrogen of the acridane ring, since decomposition of a dioxetane function with light emission is known to be facilitated by electron transfer from a neighboring hetero atom such as nitrogen (chemically initiated electron exchange luminescence: CIEEL mechanism).[4]

¶ This paper is dedicated to Professor Koji Nakanishi on the occasion of his 75th birthday.

For this purpose, we selected an acetate ester group and an aryl group: the acetate ester group would decrease an electron density by an inductive effect and the aryl group would delocalize a lone pair of the nitrogen by a mesomeric effect (Figure 1). In addition, since both groups can loose most of the electron-withdrawing property by bearing a formal negative charge (carboxylate anion and phenoxy anion), they were expected to work as a trigger for chemiluminescence *via* a CIEEL mechanism by suitable chemical treatment. In a previous paper, we demonstrated that the dioxetanes (**1**) having an acridane-*N*-acetate structure behave as expected.[5] In this paper, we describe synthesis, thermal stability, and chemiluminescence of the dioxetanes (**2**) having a *N*-arylacridane structure.



Scheme 1

Synthesis of the dioxetanes (**2**) was achieved as shown in Scheme 1. Acridones having an oxygen substituents on the benzene ring were obtained from *N*-phenylanthranilic acid (**3**) as follows. The Ullmann reaction of **3** with 4-iodoanisole afforded **4**. Treatment of **4** with sulfuric acid afforded a mixture of *N*-4-methoxyphenyl and *N*-phenyl derivatives (**5a**) and (**5b**) (*ca.* 1 : 1), recrystallization of which gave **5a** as a pure crystalline form. Compound (**5a**) was coupled with adamantanone under conditions of the McMurry reaction[6] to afford the olefin (**6a**) in good yield. After demethylation of **6a**, phenol (**6b**) was derivered to the respective *tert*-butyldimethylsilyloxy (TBDMSO), acetoxy and benzoyloxy derivatives (**6c**, **d** and **e**), respectively, according to the usual methods. Unsubstituted olefin (**6f**) was also prepared from *N*-phenylacridone (**5c**)[7] according to the same procedure. Photo-oxygenation of these olefins (**6a-f**) in the presence of polymer supported Rose-Bengal as a sensitizer under irradiation with a Na-lamp (1000 W) at -78 °C afforded the desired dioxetanes (**2**) in almost quantitative yields.[8] The structures of **2a-f** were confirmed from spectral evidences: molecular ion (M^++H) peaks were observed in their FAB-MS spectra and two carbons of the dioxetane ring appeared around 98 and 87 ppm in the ^{13}C NMR spectra. Differently from the dioxetanes (**1**) having a *N*-acetate group,[5] these compounds (**2**) were too unstable to be purified by silica gel column chromatography and were easily decomposed to adamantanone and the corresponding acridones, respectively. We, however, investigated their thermal and chemiluminescent property without purification, since the products (**2**) were shown to be pure enough for this purpose by their ^{1}H NMR spectra.

Table 1. Thermal parameters for dioxetanes (**2**) and (**7**)

Dioxetane	R	*Ea* (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	*k* (at 25 °C) ($\times 10^{-8}$/sec)	$t_{1/2}$ (at 25°C) (month)
2a	OMe	24.2	23.3	-13.2	6.92	3.9
2b	OH	22.5	21.7	-17.8	9.90	2.7
2c	OTBDMS	22.6	21.9	-17.0	9.14	2.9
2d	OAc	24.0	22.4	-16.1	5.84	4.6
2e	OBz	25.5	24.8	-10.0	5.40	5.0
2f	H	23.7	23.6	-12.8	6.89	3.9
7	–	24.5	23.9	-12.7	10.0	2.7

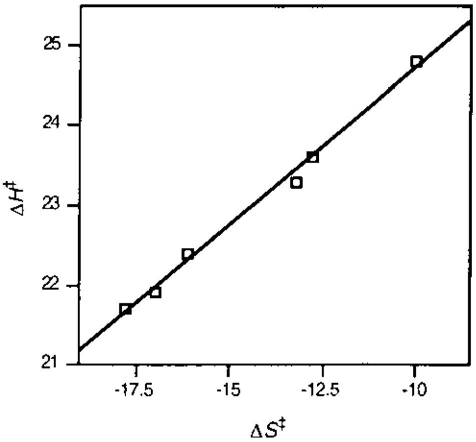


Figure 2. Isokinetic relationship for the decomposition of **2**

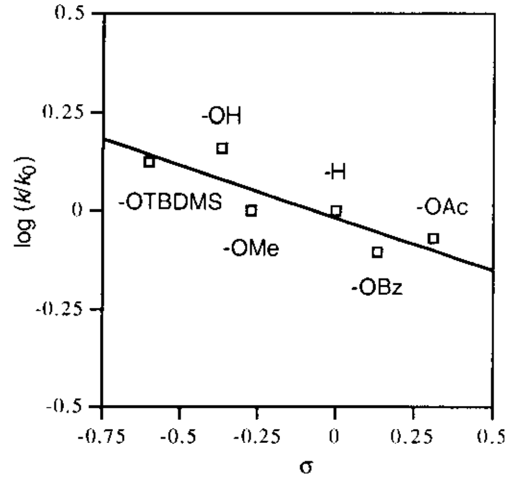
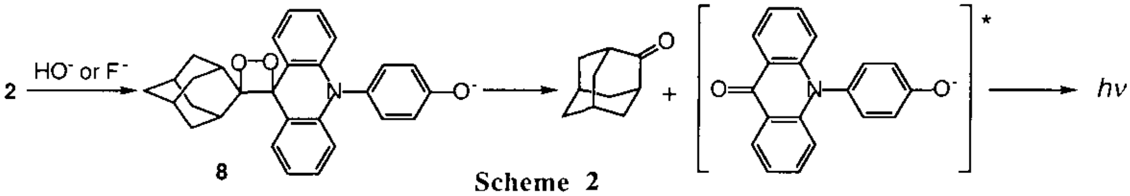


Figure 3. Hammett plots for the decomposition of **2** ($k_0 = k$ for **2** at 25 °C)

At first, thermal stability of the dioxetanes (**2**) and *N*-methyl derivative (**7**)[9,10] in *o*-xylene was examined at several temperatures (70-110 °C) by means of UV analysis. The reaction was first order over the entire temperature range studied. From the results, thermal parameters were obtained and are summarized in Table 1. The values of activation energy *Ea* of these compounds (**2**) showed that these compounds are rather unstable.[3a,11] In addition, the half-lives ($t_{1/2}$) were estimated to be in a range of 3 to 5 months at 25 °C and were roughly the same as that of *N*-methyl derivative (**7**). This suggests that the expected stabilization effect of the aryl groups does not function well. A proportional relation between the Eyring activation enthalpy $\Delta H^{\ddagger}$ and activation entropy $\Delta S^{\ddagger}$ (isokinetic relationship) was observed with a good correlation ($r^2 > 0.99$) as shown in Figure 2, showing that, regardless of the substituents, the thermal decomposition of **2** would proceed *via* a similar mechanism. On application of the Hammett rule, a negative but small slope (-0.27) was obtained as shown in Figure 3, indicating that the electron-withdrawing group on the benzene ring would stabilize the dioxetane ring as expected but not so much. In addition, the fact that good correlation was not obtained in the Hammett plots ($r^2 = 0.87$) suggests that the decomposition is affected not only by the electronic effect but also by another factor. Naturally, these matters are thought to be deeply related with the unexpectedly lower stability of **2** described above. Taking all these facts into account, the conformation of the aryl group appears to be the most responsible. As a consequence of steric repulsion between the peri-hydrogens of the acridane structure and the aryl group, these two rings would not be able to conjugate each other sufficiently as shown in conformation (**9**) (Figure 5), which would reduce electronic effect of the aryl group largely.



Scheme 2

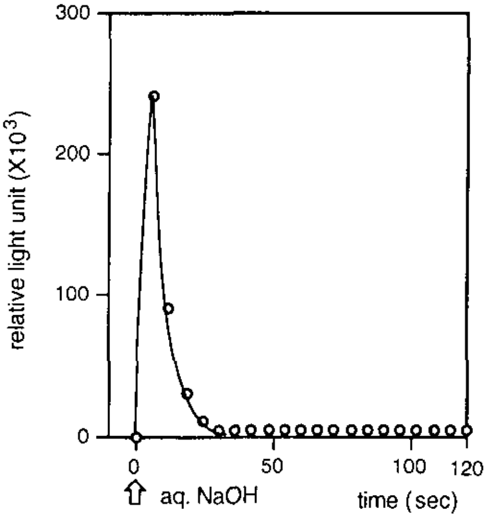
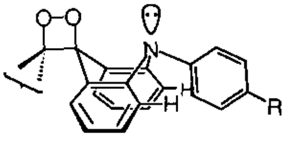


Figure 4 Light-emission pattern for **2d** induced by alkaline treatment

Table 2 Chemiluminescent quantum yields for dioxetanes (**2**)

Dioxetane	Φ_{CL} ($\times 10^{-6}$)
2b	4.2
2c	0.43
2d	3.5
2e	1.5

The chemiluminescent yields were calculated based on that of luminol ($\Phi_{CL} = 0.011$)[12]



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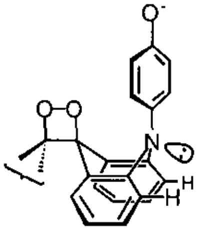

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Figure 5 Possible conformations of dioxetanes

Since stabilization effect of the aryl group was weak but was proved to exist, we examined their chemiluminescent property induced by formation of phenoxy anion as illustrated in Scheme 2. As shown in Figure 4, hydrolytic treatment of acetoxy derivative (**2d**) was found to induce light emission immediately. Benzoyl derivative (**2e**) and phenol derivative (**2b**) also showed light emission by a similar alkaline treatment. The chemiluminescent quantum yields obtained from **2b**, **d** and **e** were in a range of those reported for the other dioxetanes.[4c] On the other hand, in case of **2c**, only a weak light emission was observed by cleavage of a silyloxy bond with fluoride ion.[13]

In conclusion, although the stability and the chemiluminescent intensity of the *N*-arylacridane derivatives (**2**) were not satisfactory, these studies afforded following suggestive results. i) Despite that the *N*-aryl group cannot stabilize the dioxetane ring as does the acetate group,[5] the formation of a negative charge can trigger the chemiluminescence. This finding could be explained by taking account of partial conjugation between the nitrogen electron-pair and the aryl group in conformation (**9**) but also suggests that the electron transfer initiating the chemiluminescence might occur through space *via* conformation (**10**) (Figure 5) as well. ii) Although the chemiluminescence from **2b**, **c**, **d** and **e** is thought to take place involving a common intermediate (**8**), these compounds, particularly **2c**, afforded different intensity. These results will be significant and useful for design of more potent chemiluminescent compounds possessing a trigger function.

EXPERIMENTAL SECTION

All melting points were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR-200 infrared spectrometer. ^{1}H NMR spectra were measured on a Varian VXR-200 (200 MHz) or a JEOL EX-270 (270 MHz) spectrometer with tetramethylsilane as an internal standard; ^{13}C NMR spectra on a JEOL EX-270 (67.8 MHz) with $CDCl_3$ as an internal standard (77.0 ppm). Low and High resolution electron impact mass spectra (EI-MS and HRMS) were taken on a JEOL D-300 mass spectrometer; FAB-MS and High resolution FAB-MS on a JEOL JMS-700 mass spectrometer. UV spectra were taken on a Shimadzu UV-2100PC spectrophotometer. Chemiluminescence was measured on a Berthold Lumat LB9501 photo counter. Organic extracts were dried over anhydrous Na_2SO_4. For silica gel column chromatography, E. Merck Kieselgel 60 (0.063-0.200 mm) was used.

2-[*N*-(4-Methoxyphenyl)-*N*-phenylamino]benzoic acid (4). A mixture of *N*-phenylanthranilic acid (**3**, 10.0 g, 46.9 mmol), anhydrous K_2CO_3 (6.5 g, 47 mmol), Cu powder (0.24 g, 1.9 mmol) and 4-iodoanisole (13.2 g, 56.4 mmol) in nitrobenzene (150 mL) was heated at 200 °C under stirring for 8 h. The reaction mixture was cooled and then steam-distilled. The distillate was acidified with 10% HCl and was kept cooling. The resultant crystalline precipitate was collected by filtration and purified by silica gel column chromatography ($CHCl_3$: MeOH = 20 : 1) to afford the title compound (4.4 g, 65%) as yellow crystals, mp 152.5-154 °C (EtOH); IR ν (KBr): 3036, 1696, 1593, 1507, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 3.76 (3H, s), 6.79 (2H, d, J = 7 Hz), 6.87 (2H, d, J = 7 Hz), 6.98 (3H, t, J = 7 Hz), 7.15-7.20 (3H, m), 7.25 (1H, t, J = 7 Hz), 7.50 (1H, t, J = 7 Hz), 7.98 (1H, t, J = 7 Hz), 8.75-12.5 (1H, br); ^{13}C NMR ($CDCl_3$) δ: 55.4, 114.6, 121.5, 122.2, 125.0, 125.9, 127.0, 129.1, 129.3, 132.3, 133.7, 140.4, 147.6, 148.3, 156.2, 169.4; EI-MS *m/z*: 319 (M^+, 100); *Anal.* Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 74.93; H, 5.44; N, 4.35.

10-(4-Methoxyphenyl)-9(10*H*)-acridone (5a). A solution of the acid (4) (10 g, 31 mmol) in conc. H_2SO_4 (15 mL) was heated at 90 °C under stirring for 2 h. The reaction mixture was poured into ice-water and the resultant precipitate was collected by filtration, washed with cold water and purified by silica gel column chromatography ($CHCl_3$: MeOH = 80 : 1) to afford a mixture of **5a** and **b** (*ca.* 1 : 1, 9.40 g, 75%), which was recrystallized from EtOH to give **5a** (2.75 g, 22%) as yellow needles, mp 238-239.5 °C (EtOH), IR ν (KBr): 2252, 1651, 1557, 1505, 1023 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 393 (13000), 374 (10000), 250 (51000); ^{1}H NMR ($CDCl_3$) δ: 3.95 (3H, s), 6.82 (2H, d, *J* = 9 Hz), 7.16-7.31 (6H, m), 7.50 (2H, td, *J* = 8, 2 Hz), 8.58 (2H, dd, *J* = 8, 2 Hz); ^{13}C NMR ($CDCl_3$) δ: 55.6, 116.1, 116.9, 121.4, 121.8, 127.2, 130.9, 131.2, 133.2, 143.4, 160.1, 178.1; EI-MS *m/z*: 301 (M$^+$, 100), 286 (M$^+$-Me, 30); *Anal.* Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.73; H, 4.98; N, 4.65.

9,10-Dihydro-10-(4-methoxyphenyl)-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6a). Under a nitrogen atmosphere, $LiAlH_4$ (383 mg, 10.1 mmol) was added in portions to a stirred suspension of anhydrous $TiCl_3$ (4.00 g, 20.1 mmol) in THF (20 mL) under ice-cooling and stirring was continued at the same temperature for 10 min. After addition of triethylamine (0.735 mL, 10.1 mmol) at rt, the reaction mixture was refluxed for 1 h. A solution of acridone (**5a**) (620 mg, 2.05 mmol) and adamantanone (308 mg, 2.05 mmol) in THF (15 mL) was added dropwise to the stirred reaction mixture for 30 min under reflux and the whole mixture was kept stirring under reflux for 17 h. After cooling with an ice-bath, the reaction was quenched with water and the reaction mixture was extracted with AcOEt. The organic layer was washed with water and saturated NaCl solution, dried and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 1 : 1) to afford the olefin (**6a**) (723 mg, 84%) as colorless crystals, mp 237-239 °C (EtOH); IR ν (KBr): 2906, 1587, 1510, 1451, 1246, 1035 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 340 (6900), 258 (21000), 227 (42000); ^{1}H NMR ($CDCl_3$) δ: 1.87-2.04 (12H, m), 3.49 (2H, br s), 3.88 (3H, s) 6.46 (2H, dd, *J* = 7, 2 Hz), 6.92-6.99 (4H, m), 7.09 (2H, d, *J* = 9 Hz), 7.22-7.30 (4H, m); ^{13}C NMR ($CDCl_3$) δ: 28.1, 32.1, 37.1, 39.6, 55.5, 113.7, 115.5, 119.7, 123.9, 125.8, 127.2, 132.2, 133.2, 144.6, 144.7, 159.1; EI-MS *m/z*: 419 (M$^+$, 100); *Anal.* Calcd for $C_{30}H_{29}NO$: C, 85.88; H, 6.97; N, 3.34. Found: C, 85.62; H, 6.97; N, 3.31.

The olefin (**6f**) was prepared from **5c** according to the same method as described above.

9,10-Dihydro-10-phenyl-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6f), 51% yield, colorless crystals, mp 254.5-255.5 °C (AcOEt); IR ν (KBr): 2906, 2846, 1466, 1452, 1278, 751 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 340 (10000), 286 (15000), 256 (21000), 228 (47000); ^{1}H NMR ($CDCl_3$) δ: 1.80-2.10 (12H, m), 3.50 (2H, br s), 6.44 (2H, dd, *J* = 8, 1 Hz), 6.85-7.05 (4H, m), 7.20-7.35 (2H, m), 7.39 (2H, dd, *J* = 7, 1 Hz), 7.49-7.65 (3H, m); ^{13}C NMR ($CDCl_3$) δ: 28.7, 32.1, 37.1, 39.7, 113.8, 120.0, 124.1, 125.8, 127.3, 128.1, 130.4, 131.3, 140.8, 144.4, 144.8; EI-MS *m/z*: 389 (M$^+$, 100); *Anal.* Calcd for $C_{29}H_{27}N$: C, 89.42; H, 6.99; N, 3.60. Found: C, 89.31; H, 7.24; N, 3.62.

9,10-Dihydro-10-(4-hydroxyphenyl)-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6b). A suspension of **6a** (110 mg, 0.262 mmol) in 47% HBr (2.5 mL) was refluxed for 24 h under stirring. The reaction mixture was neutralized with 50% NaOH solution and extracted with AcOEt. The combined organic layer was washed with water and saturated NaCl solution, dried, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt : hexane = 1 : 1) to afford the title compound (**6b**) (104 mg, 98%) as colorless crystals, mp 137-139 °C (EtOH); IR ν (KBr):

2907, 1587, 1512, 1451, 1278, 752 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 342 (7700), 256 (15000); ^{1}H NMR ($CDCl_3$) δ: 1.80-2.20 (12H, m), 3.47 (2H, br s), 6.47 (2H, dd, J = 8, 2 Hz), 6.96 (4H, td, J = 7, 1 Hz), 7.05 (2H, dd, J = 8, 2 Hz), 7.20-7.27 (4H, m); ^{13}C NMR ($CDCl_3$) δ: 28.0, 32.1, 37.1, 39.6, 113.7, 117.0, 119.6, 119.9, 123.9, 125.8, 127.2, 132.4, 133.1, 144.7, 155.4; EI-MS *m/z*: 405 (M$^+$, 100); *Anal.* Calcd for $C_{29}H_{27}NO{\cdot}EtOH$: C, 82.45; H, 7.37; N, 3.10. Found: C, 82.29; H, 7.42; N, 3.05.

9,10-Dihydro-10-[4-(*tert*-butyldimethylsilyloxy)phenyl]-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6c). To a stirred solution of **6b** (110 mg, 0.383 mmol) in DMF (1.0 mL) were added TBDMSCl (72.0 mg, 0.478 mmol) and imidazole (48.0 mg, 0.705 mmol) and the whole was stirred at rt for 5 h. The reaction mixture was diluted with ether, washed with water, dried, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography ($CHCl_3$: MeOH = 25 : 1) to afford the title compound (**6c**) (90.0 mg, 59%) as light yellow needles, mp 202-203 °C (AcOEt); IR ν (KBr): 2932, 1639, 1604, 1507, 1489, 1459, 1266, 923, 743 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 340 (9000), 288 (10000), 256 (18000); ^{1}H NMR ($CDCl_3$) δ: 0.29 (6H, s), 1.04 (9H, s), 1.88-2.05 (12H, m), 3.49 (2H, br s), 6.48 (2H, dd, J = 8, 1 Hz), 6.91-7.07 (6H, m), 7.21-7.25 (4H, m); ^{13}C NMR ($CDCl_3$) δ: -4.4, 18.2, 25.7, 28.1, 32.1, 37.1, 39.7, 113.7, 119.7, 119.9, 121.7, 124.0, 125.8, 127.2, 132.2, 133.8, 144.7, 155.3. EI-MS *m/z*: 519 (M$^+$, 5), 91 (100); *Anal.* Calcd for $C_{35}H_{41}NOSi$: C, 80.87; H, 7.95; N, 2.69. Found: C, 80.87; H, 8.08; N, 2.71.

9,10-Dihydro-10-(4-acetoxyphenyl)-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6d). To a stirred solution of **6b** (415 mg, 1.02 mmol) in pyridine (3 mL) was added acetic anhydride (0.120 mL, 1.27 mmol) and the whole was stirred at rt for 8 h. The reaction mixture was poured into saturated $NaHCO_3$ solution containing ice and extracted with $CHCl_3$. The combined organic layer was washed successively with water, 10% HCl, water and saturated NaCl solution, dried and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography to afford the title compound (**6d**) (403 mg, 88%) as colorless crystals, mp 208-210 °C (AcOEt); IR ν (KBr): 2907, 1762, 1588, 1507, 1452, 1275, 1197 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 340 (9000), 290 (1000), 256 (18000); ^{1}H NMR ($CDCl_3$) δ: 1.80-2.10 (12H, m), 2.35 (3H, s), 3.48 (2H, br s), 6.45 (2H, dd, J = 7, 2 Hz), 6.85-7.10 (4H, m), 7.25 (2H, dd, J = 7, 2 Hz), 7.35 (4H, d, J = 5 Hz); ^{13}C NMR ($CDCl_3$) δ: 21.2, 28.0, 32.1, 37.1, 39.6, 113.8, 119.6, 120.1, 123.5, 124.1, 125.9, 127.2, 132.2, 138.1, 144.3, 144.9, 150.1, 169.2; EI-MS *m/z*: 447 (M$^+$, 100). *Anal.* Calcd for $C_{31}H_{29}NO_2$: C, 83.19; H, 6.53; N, 3.13. Found: C, 82.98; H, 6.63; N, 3.13.

9,10-Dihydro-10-(4-benzoyloxyphenyl)-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6e). To a stirred suspension of **6b** (430 mg, 1.06 mmol) in CH_2Cl_2 (2 mL) and triethylamine (1.0 mL, 7.2 mmol) was added benzoyl chloride (0.15 mL, 1.29 mmol) under ice-cooling and the whole was stirred at rt for 7 h. The reaction mixture was worked up according to a similar procedure to that described for **6d** and the crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 2) to give the title compound (**6e**) (461 mg, 85%) as colorless crystals, mp 220-221.5 °C (AcOEt); IR ν (KBr): 3068, 2905, 1743, 1587, 1506, 1451, 1262, 1200, 1060 cm^{-1}; UV λ_{max}^{MeCN} nm (ε): 338 (9300), 288 (11000), 228 (58000); ^{1}H NMR ($CDCl_3$) δ: 1.80-2.10 (12H, m), 3.50 (2H, br s), 6.51 (2H, dd, J = 8, 2 Hz), 6.90-7.10 (4H, m), 7.27 (2H, dd, J = 7, 2 Hz), 7.35-7.75 (7H, m), 8.26 (2H, dd, J = 8, 2 Hz); ^{13}C

NMR ($CDCl_3$) δ: 28.0, 32.1, 37.1, 39.6, 113.8, 119.6, 120.2, 123.7, 124.1, 125.9, 127.3, 128.7, 129.3, 130.2, 132.4, 138.3, 144.3, 144.9, 150.4, 165.0; EI-MS *m/z*: 509 (M^+, 100); *Anal.* Calcd for $C_{36}H_{31}NO_2$: C, 84.84; H, 6.13; N, 2.75. Found: C, 84.81; H, 6.27; N, 2.84.

Photo-oxygenation of olefins (6). To a mixture of polymer supported Rose-Bengal[8] (200 mg) and a solution of olefin **6** (0.11 mmol) in CH_2Cl_2 (15 mL) was passed oxygen at -78 °C under irradiation with a Na lamp (1000 W) for 2 h. The polymer was filtered off and washed with CH_2Cl_2 and the filtrate was concentrated at 0 °C under reduced pressure to afford the dioxetane (**2**) as a light yellow powder in quantitative yield. Spectral properties of **2** are as follows.

10-(4-Methoxyphenyl)dispiro[acridine-9(10*H*),3'-[1,2]dioxetane-4',2"-tricyclo-[3.3.1.1^{3,7}]decane] (2a). ^1H NMR ($CDCl_3$) δ: 0.86 (2H, br d, *J* = 13 Hz), 1.20-2.10 (10H, m), 2.33 (2H, br s), 3.91 (3H, s), 6.45 (2H, dd, *J* = 7, 1 Hz), 7.05-7.35 (8H, m), 8.24 (2H, dd, *J* = 6, 2 Hz); ^{13}C NMR ($CDCl_3$) δ: 25.6, 25.7, 31.8, 33.0, 36.2, 55.6, 86.7, 98.2, 113.5, 116.0, 119.0, 120.3, 128.3, 128.7, 131.7, 132.3, 140.8, 159.5; FAB-MS *m/z*: 452 (M^++H); High-resolution FAB-MS: Calcd for $C_{30}H_{30}NO_3$ (M^++H): 452.2226; Found: 452.2249.

10-(4-Hydroxyphenyl)dispiro[acridine-9(10*H*),3'-[1,2]dioxetane-4',2"-tricyclo-[3.3.1.1^{3,7}]decane] (2b). ^1H NMR ($CDCl_3$) δ: 0.82-0.92 (2H, m), 1.20-2.20 (10H, m), 2.26-2.34 (2H, m), 5.20 (1H, br s), 6.41-6.45 (2H, m), 6.86-7.23 (8H, m), 8.24 (2H, dd, *J* = 5, 2 Hz); ^{13}C NMR ($CDCl_3$) δ: 25.6, 27.4, 31.6, 31.7, 33.0, 36.2, 47.0, 81.9, 98.2, 113.4, 114.0, 117.6, 120.3, 128.3, 128.7, 132.3, 140.8, 155.7; FAB-MS *m/z*: 438 (M^++H).

10-[4-(*tert*-Butyldimethylsilyloxy)phenyl]dispiro[acridine-9(10*H*),3'-[1,2]dioxetane-4',2"-tricyclo[3.3.1.1^{3,7}]decane] (2c). ^1H NMR ($CDCl_3$) δ: 0.29 (6H, s), 0.85 (2H, br d, *J* = 13 Hz), 1.04 (9H, s), 1.20-2.20 (10H, m), 2.33 (2H, br s), 6.45 (2H, dd, *J* = 7, 1 Hz), 7.00-7.25 (8H, m), 8.24 (2H, dd, *J* = 6, 2 Hz); ^{13}C NMR ($CDCl_3$) δ: -4.3, 18.2, 25.6, 31.7, 33.0, 36.2, 86.7, 98.2, 113.4, 119.0, 120.3, 122.2, 128.3, 128.7, 131.7, 132.8, 140.8, 155.8; FAB-MS *m/z*: 552 (M^++H); High-resolution FAB-MS: Calcd for $C_{35}H_{42}NO_3Si$ (M^++H): 552.2934; Found: 552.2932.

10-(4-Acetoxyphenyl)dispiro[acridine-9(10*H*),3'-[1,2]dioxetane-4',2"-tricyclo-[3.3.1.1^{3,7}]decane] (2d). ^1H NMR ($CDCl_3$) δ: 0.84 (2H, br d, *J* = 13 Hz), 1.24 (2H, br d, *J* = 13 Hz), 1.35-1.60 (5H, m), 1.66 (1H, br s), 1.84 (2H, br d, *J* = 13 Hz), 2.33 (2H, br s), 2.38 (3H, s), 6.44 (2H, dd, *J* = 5, 2 Hz), 7.12-7.28 (6H, m), 7.34-7.39 (2H, m), 8.25 (2H, dd, *J* = 4, 2 Hz); ^{13}C NMR ($CDCl_3$) δ: 21.2, 25.5, 25.6, 31.7, 33.0, 36.1, 86.6, 98.1, 113.4, 119.1, 120.6, 124.1, 128.4, 128.8, 131.9, 137.2, 140.4, 150.5, 169.1; FAB-MS *m/z*: 480 (M^++H); High-resolution FAB-MS: Calcd for $C_{31}H_{31}NO_4$ (M^++H): 480.2174; Found: 480.2198.

10-(4-Benzoyloxyphenyl)dispiro[acridine-9(10*H*),3'-[1,2]dioxetane-4',2"-tricyclo-[3.3.1.1^{3,7}]decane] (2e). ^1H NMR ($CDCl_3$) δ: 0.87 (2H, br d, *J* = 12 Hz), 1.25-2.20 (10H, m), 2.37 (2H, br s), 6.51 (2H, dd, *J* = 6, 2 Hz), 7.15-7.80 (11H, m), 8.29 (2H, dd, *J* = 6, 2 Hz); ^{13}C NMR ($CDCl_3$) δ: 25.5, 25.6, 31.7, 33.0, 36.1, 86.6, 98.2, 113.5, 119.2, 120.6, 124.3, 128.4, 128.7, 128.8, 129.1, 130.3, 132.0, 133.9, 137.3, 140.4, 150.9, 164.9; FAB-MS *m/z*: 542 (M^++H); High-resolution FAB-MS: Calcd for $C_{36}H_{32}NO_4$ (M^++H): 542.2332; Found: 542.2354.

10-Phenyldispiro[acridine-9(10*H*),3'-[1,2]dioxetane-4',2"-tricyclo-[3.3.1.1^{3,7}]decane]

(2f). ^{1}H NMR ($CDCl_3$) δ: 0.88 (2H, br d, J = 13 Hz), 1.20-2.20 (10H, m), 2.33 (2H, br s), 6.41 (2H, dd, J = 2, 5 Hz), 7.10-7.30 (6H, m), 7.45-7.70 (3H, m), 8.26 (2H, dd, J = 4, 3 Hz); ^{13}C NMR ($CDCl_3$) δ: 25.6, 25.7, 31.8, 33.0, 36.2, 55.6, 86.7, 98.2, 113.5, 116.0, 119.0, 120.3, 128.3, 128.7, 131.7, 132.3, 140.8, 159.5; FAB-MS *m/z*: 422 (M^++H); High-resolution FAB-MS: Calcd for $C_{29}H_{28}NO_2$ (M^++H): 422.2120; Found: 422.2137.

Thermal decomposition of dioxetanes (2). A quartz cell containing a solution of dioxetane (**2**) in *o*-xylene (*ca.* 0.75 mM) was placed in a UV spectrometer, temperature in the cell-holder of which had been maintained at constant temperature (110, 100, 90, 80 and 70 °C) with a Pertie thermocontroller. The decomposition reaction was immediately traced by monitoring the formation of the corresponding acridone at 250 nm and first order rate constants of the thermal decomposition of **2** at each temperature were obtained (Table 3).

Table 3. Rate constants (10^{-4} sec^{-1}) for the decomposition of dioxetanes (**2**) in *o*-xylene

Dioxetane	R	Temperature (°C)				
		110	100	90	80	70
2a	OMe	5.39	2.75	1.11	0.400	0.139
2b	OH	4.77	2.06	0.940	0.398	0.143
2c	OTBDMS	5.41	2.87	1.20	0.461	0.152
2d	OAc	4.23	2.14	0.897	0.323	0.111
2e	OBz	3.39	1.54	0.571	0.271	0.062
2f	H	4.71	2.39	0.911	0.353	0.130

Chemiluminescent activity of dioxetanes (2). The luminescence was induced by the addition of a DMSO (0.1 mL) solution of dioxetane **2** to a solution of NaOH (0.1 M, 0.3 mL, for **2d** and e) or tetrabutylammonium fluoride (0.01 M, 0.1 mL, for **2c**) at rt and was monitored and integrated for 120 sec. The chemiluminescent quantum yields, calculated on the basis of that of luminol (Φ_{CL} = 0.011),[12] and the light emission pattern for **2d** are shown in Table 2 and Figure 4, respectively.

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9. The *N*-methyl derivative (**7**) was obtained as a light yellow powder from *N*-methylacridone according to the same method as described for **2**. Literatures describing the synthesis of **7** are as follows: a) F. McCapra, I. Beheshti, A. Burford, R. A. Hann, and K. A. Zakilica, *J. Chem. Soc., Chem. Commun.*, **1977**, 945; b) F. McCapra and D. Watmore, *Tetrahedron Lett.*, 1982, **23**, 5225.
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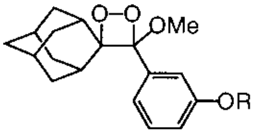
13. In contrast to our present result, it was reported that, in the chemiluminescence from dioxetane derivatives (**11**), the chemiluminescent intensity induced by cleavage of a silyloxy bond in a dry organic solvent was particularly strong and was estimated to be *ca.* 20000 times greater than that induced by hydrolytic cleavage of a phosphate ester in an aqueous system.[2b,4b]



11: R = TBDMS or PO_3Na_2

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