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Oxiranes having an acridane structure as a novel chemiluminescent precursor: synthesis and chemiluminescent studies

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Abstract—Oxirane derivatives having acridane and adamantane structures were designed as a novel chemiluminescent precursor and were found to have a characteristic chemiluminescent ability which is introduced by a two-step trigger reaction involving treatment with alkaline H_2O_2 and subsequent acidic treatment. Structural study of the oxirane derivatives showed that the CIEEL mechanism is involved in this chemiluminescent reaction and it was also found that the chemiluminescent profile is affected by the kind of acid employed in the trigger reaction.

1. Introduction

An analytic method using chemiluminescent compounds has attracted much attention as a promising tool for detection of a small quantity of biomacromolecules.[1] Intensive studies on various chemiluminescent peroxy derivatives such as 1,2-dioxetanes have been reported[2] and, in fact, some 1,2-dioxetane derivatives are known to exhibit high light-emission ability. However, there still remain problems to be resolved before they can be employed as a versatile method: the level of their stability does not permit easy handling. For such purposes, the compound would desirably be stable enough and, in addition, would desirably be designed not only as to be able to induce strong chemiluminescence by a trigger reaction, but also as to be able to control the chemiluminescent profile by the reaction conditions or by an inherent property of the compound.

Sakanishi and his co-workers reported an interesting example, namely, that light emission was observed during the oxidation of 9-arylmethylene-10-methylacridane **1** with an excess of *m*-chloroperbenzoic acid (*m*-CPBA) or dimethyldioxirane (DMD).[3] They proposed that β-hydroxyalkyl peroxyesters or 1,2,4-trioxanes generated in situ via unstable oxiranes **2** are involved as the key intermediates and would be decomposed via a chemically initiated electron exchange luminescence (CIEEL) mechanism. It occurred to us that an oxirane ring system could be stabilized by introducing a bulky substituent, such as an adamantane moiety,[4] thereby rendering it a more potent precursor for chemiluminescence than a dioxetane ring system.[5] According to this idea, we designed some oxirane derivatives **3** and herein describe the preparation of these oxiranes **3a**–**f** and their chemiluminescence which is specifically induced by a unique trigger reaction involving oxidative treatment followed by acidic treatment (Fig. 1).[6]

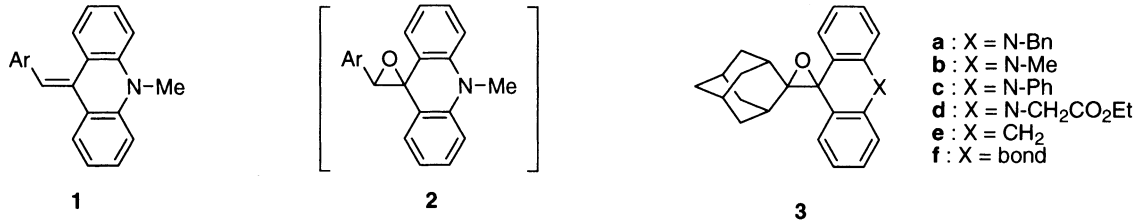

Figure 1. Structures of compounds **1**–**3**.

Keywords: chemiluminescence; oxiranes; epoxides; dioxetanes.
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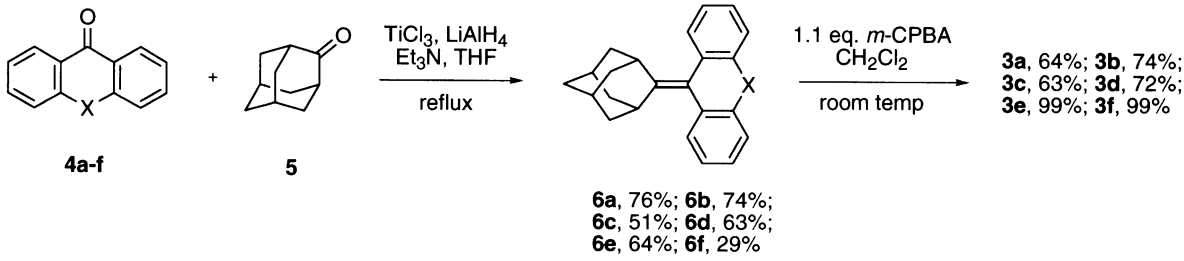


Scheme 1.

Table 1. Chemiluminescent intensity for the oxiranes **3a–f**

Run	Oxirane **3**[a]	Additive (at 0 s)[b]	Amounts of HCl (at 25 s)	TRLU ($\times 10^3$)[c]
1	**3a**	*m*-CPBA in CH_2Cl_2	None	<10
2	**3a**	Alkaline H_2O_2	None	<10
3	**3a**	Alkaline H_2O_2	0.10 M, 0.1 ml	3065
4	**3b**	Alkaline H_2O_2	0.10 M, 0.1 ml	2047
5	**3c**	Alkaline H_2O_2	0.10 M, 0.1 ml	320
6	**3d**	Alkaline H_2O_2	0.10 M, 0.1 ml	57
7	**3e**	Alkaline H_2O_2	0.10 M, 0.1 ml	<10
8	**3f**	Alkaline H_2O_2	0.10 M, 0.1 ml	26

[a] A solution of **3** in DMSO (1.0×10^{-7} M, 0.10 ml) was used.
[b] A solution of H_2O_2 in 0.1 M aqueous NaOH (0.1 M, 0.1 ml) was used.
[c] Total relative light units (TRLU) integrated for 120 s.

2. Results and discussion

The oxirane derivatives **3** were easily synthesized as follows. Olefins **6** were obtained by the McMurry reaction of aromatic ketones **4** with 2-adamantanone (**5**). The olefins **6** were treated with a slight excess of *m*-CPBA in dichloromethane at room temperature, giving oxiranes **3** in good yields. Although isolation of the oxiranes **2** was reported to be impossible,[3] the oxiranes **3a–f** were able to be purified by silica gel column chromatography and were quite stable allowing handling under ambient conditions as expected (Scheme 1).

At first, the luminescent property of **3a** was examined, and the results are outlined in Table 1. According to Sakanishi's report, [3a]oxirane **3a** was further oxidized with *m*-CPBA in various solvent systems. However, remarkable light emission was not detectable under the conditions (run 1). On treatment of **3a** with an alkaline hydrogen peroxide (H_2O_2) solution, rapid decomposition was observed on the TLC, but in this case as well there was no intense chemiluminescence (run 2). On the other hand, when hydrochloric acid was added after 25 s delay from the alkaline H_2O_2 treatment, quick and strong light emission was detectable as shown in Fig. 2 (run 3) accompanying the formation of ketones **4a** and **5**. The chemiluminescent intensity was not affected by the delay time in a range 20–180 s. In order to investigate the effect of the nitrogen at X, the other oxiranes **3b–f** were also examined under the same conditions (runs 4–8). The oxiranes **3b–f** were also decomposed rapidly by treatment with alkaline H_2O_2. The chemiluminescent intensity of the *N*-methyl derivative **3b** was weaker than that of **3a**. The introduction of an electron-withdrawing group on the nitrogen (**3c** and **d**), however, further decreased the light emission (runs 5 and 6). The compounds **3e** and **f**, neither of which has a nitrogen, were almost inert (runs 7 and 8). These findings indicate the significant role of the electron-donating property of the nitrogen for the chemiluminescence.

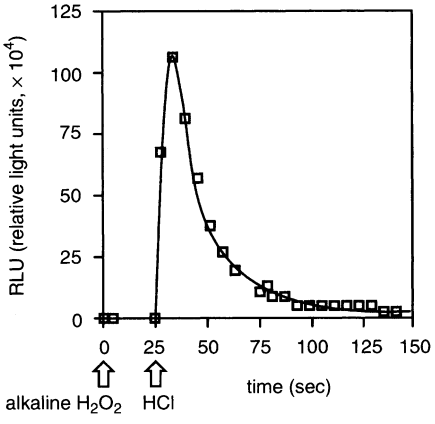


Figure 2. Light-emission profiles of **3a** in DMSO by treatment with alkaline H_2O_2 and subsequent with HCl.

The amount of HCl was also found to affect the intensity of the light emission. When 1 equiv. of the acid to the base was added, the strongest light emission was obtained as shown in Fig. 3. The chemiluminescent quantum yield (Φ_{CL}) was estimated to be 0.0018, based on that of luminol (Φ_{CL}=0.011) and is ca. 4000 times stronger than that of the olefin **1** (Ar=Ph) reported by Sakanishi.[3a] The use of excess HCl drastically decreased the light emission, which is probably due to the protonation at the nitrogen by the excess HCl.

Next, we measured the chemiluminescent intensity of **3a** by

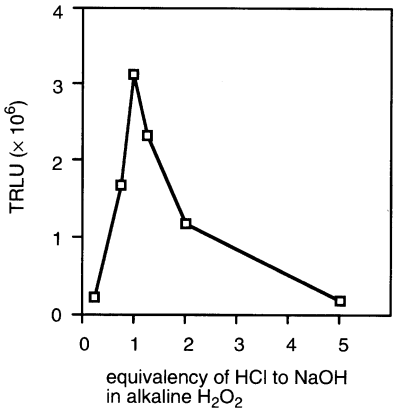


Figure 3. Relationship between the chemiluminescent intensity for **3a** in DMSO and the amount of HCl.

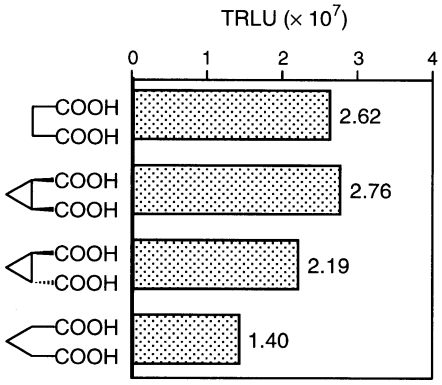


Figure 5. Chemiluminescent intensity for **3a** in dioxane induced by *cis*- and *trans*-cyclopropanedicarboxylic acids.

using various mineral and organic acids in place of HCl and found that the chemiluminescent intensity depends on the kind of acid used. Among the acids examined, oxalic acid afforded stronger chemiluminescence than did HCl. The amount of oxalic acid also affected the intensity, and the strongest chemiluminescence was observed when 2 equiv. of oxalic acid to NaOH in alkaline H_2O_2 was added. Because two factors, the acidity and structural feature, were thought to be related to this chemiluminescence, we focused on the dicarboxylic acids having a different methylene length in order to clarify this point. As shown in Fig. 4, the chemiluminescent intensity appeared to depend on the methylene length rather than the acidity. Malonic acid (n=1) was the best choice to obtain the strongest chemiluminescence.

To establish more clearly the structural influence of dicarboxylic acids, *cis*- and *trans*-1,2-cyclopropanedicarboxylic acids, regarded as conformationally restricted succinic and glutalic acids (n=2 and 3), were also examined. As shown in Fig. 5, the *cis*-acid afforded stronger chemiluminescence than the *trans*-acid. In particular, the chemiluminescent intensity by succinic acid was in the range of those by *cis*- and *trans*-acids. These results strongly suggest that the distance between the two carboxyl groups plays a significant role.

The role of the carboxyl group was then studied by replacing one of the two carboxyl groups of oxalic acid with hydroxymethyl, methyl, and aminomethyl groups, respectively (Fig. 6). Interestingly, hydroxyacetic acid afforded almost the same chemiluminescent pattern and stronger intensity upon comparison with oxalic acid. However, acetic acid was less effective and its chemiluminescent pattern was somewhat different from those of oxalic and hydroxyacetic acids. These results show that the 'OH' function increases the chemiluminescence, and the hydroxymethyl group, in place of one of the two carboxyl groups, plays the same role more effectively. In contrast, glycine afforded a quite different chemiluminescent pattern as shown. Although it was weak, detectable light-emission by a photon counter was continued even after 15 min. It is note worthy that the total value of the relative light units induced by glycine for 120 s is low, but that for 15 min approaches the value induced by oxalic acid for 120 s. This suggests that the total amount of the intermediate formed by glycine is almost the same as that by oxalic acid, only its rate is slower.[8]

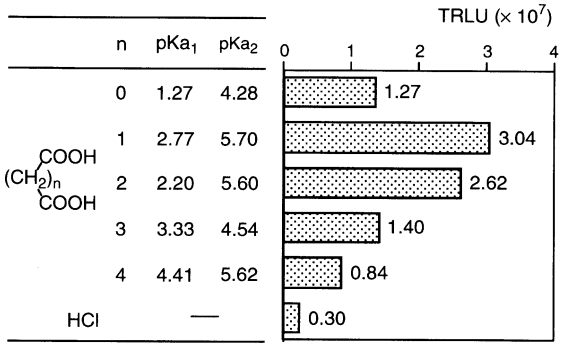
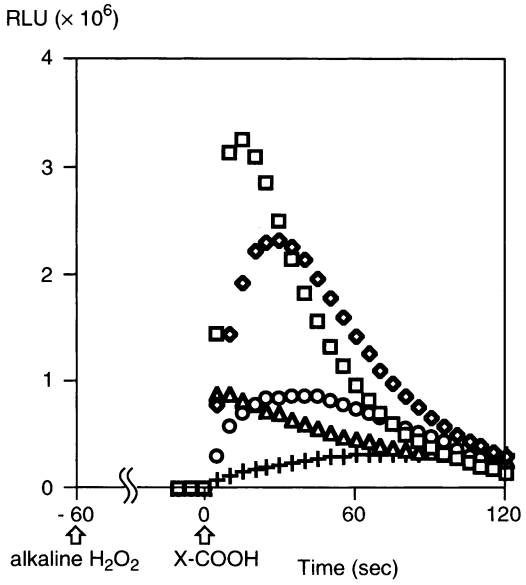


Figure 4. Relationship between pK_a values for dicarboxylic acids,[7] HOOC–$(CH_2)_n$–COOH (n=0–4) and chemiluminescent intensity of **3a** in dioxane induced by the acids.

Taking into account all the results described above, we considered the chemiluminescent process of **3a** to be as shown in Scheme 2. At first, the oxirane ring is most likely to be attacked by the hydroperoxy anion to form α-hydroperoxy alcohol **7**. The following acidic treatment of **7** would lead to the following two pathways: (i) decomposition from the *anti*-conformation *anti*-**7** could give ketones **4a** and **5**; (ii) formation of the dioxetane **8** from the *syn*-conformation *syn*-**7** could occur by participation of the neighboring hydroxy group.[9] Since a 1,2-dioxetane structure is known to be decomposed via a CIEEL mechanism to form an excited ketone which emits light,[10] the latter pathway appears to be responsible for the present chemiluminescence.[11]

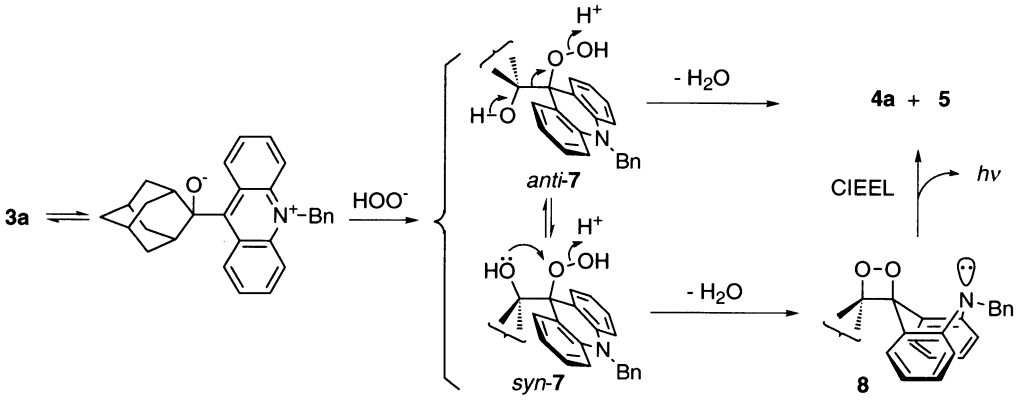
Although the details are not clear, the effect of the kind of acid used also appears to support this mechanism and could be explained as follows. The carboxylic acids having another carboxyl group or a hydroxy group in their proximity, like malonic acid and hydroxyacetic acid, could interact favorably with the *syn*-conformation of α-hydroperoxy alcohol *syn*-**7** as represented by **A** and **B** in Fig. 7 and, consequently, could increase the formation of the 1,2-dioxetane by effective H^+ transfer from the carboxyl group to the hydroperoxy group of *syn*-**7**, rather



X–COOH	TRLU for 120 sec (× 10^4)
□ : $HOOC\text{-}CH_2$-	3042
◇ : $HO\text{-}CH_2$-	2352
○ : HOOC-	1366
△ : H_3C-	1262
+ : $H_2N\text{-}CH_2$-	683 (1194)

The value in the parenthesis is TRLU integrated for 15 min.

Figure 6. Chemiluminescent profile and intensity for **3a** in dioxane induced by treatment with X–COOH.



Scheme 2.

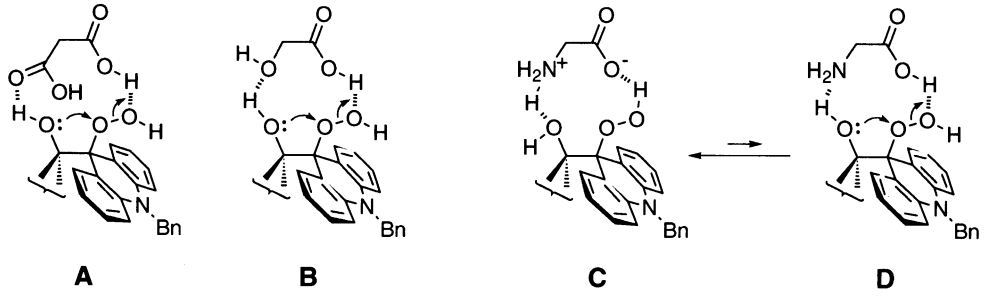


Figure 7. Proposed interaction of *syn*-**7** with malonic acid, hydroxyacetic acid or glycine.

than direct decomposition via anti-conformation of α-hydroperoxy alcohol *anti*-**7**. In contrast, glycine appears to exist as an ionized form mainly under the conditions employed, but would exist as a non-ionized form as well via equilibrium. Since interaction of the ionized form with *syn*-**7** cannot protonate the hydroperoxy function and thus, the nucleophilicity of the hydroxy group is decreased as illustrated by **C**, the 1,2-dioxetane would not be formed. In contrast, a similar interaction of the non-ionized form with *syn*-**7** could protonate and also increase the nucleophilicity of the hydroxy group of *syn*-**7** to form the 1,2-dioxetane as shown by **D**. The weak but continuous light-emission by the addition of glycine is most likely to be explained by taking the interaction of the non-ionized form gradually produced from the ionized form via the equilibrium.

In conclusion, we have demonstrated a novel example of chemiluminescence which is specifically induced from a novel precursor **3a** having an oxirane structure and an *N*-benzylacridane structure by a trigger reaction: alkaline H_2O_2 treatment and acidic treatment. The structural effect of the oxirane derivatives on the chemiluminescence showed that a CIEEL mechanism is involved in this chemiluminescence. It was also found that the chemiluminescence from the oxirane **3a** has an interesting feature namely that the chemiluminescent profile can be changed by the kind of acid used in the trigger reaction. The results shown in this paper would demonstrate the oxirane **3a** to be a potent chemiluminescent probe for the analysis of biomacromolecules.

3. Experimental

3.1. General

Melting points (mps) were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. Infrared spectra were measured on a JASCO FT/IR-200 Fourier-transfer infrared spectrometer. ^{1}H NMR spectra were measured on a JEOL EX-270 (270 MHz) spectrometer and tetramethylsilane (TMS) was used as an internal standard. ^{13}C NMR spectra were measured on a JEOL EX-270 (67.8 MHz) spectrometer with $CDCl_3$ as an internal standard (77.0 ppm). Electron-impact mass spectra (EI-MS) were obtained by use of a JEOL JMS-700 mass spectrometer. Chemiluminescent intensity was monitored on a Berthold Lumat LB 9501 photon counter. For silica gel column chromatography, E. Merck Kieselgel 60 (0.063–0.200 mm) was used. 10-Substituted 9(10*H*)-acridones **4a**,[12a] **4b**,[12a] **4c**[12b] and **4d**[12c] were prepared from 9(10*H*)-acridone according to literatures.

3.1.1. 10-Benzyl-9,10-dihydro-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6a). Under a nitrogen atmosphere, $LiAlH_4$ (383 mg, 10.1 mmol) was added to a stirred suspension of $TiCl_3$ (4.00 g, 20.1 mmol) under ice-cooling and the stirring was continued for 10 min at the same temperature. After addition of Et_3N (0.74 ml, 10.1 mmol) at room temperature, the whole was refluxed for 1 h. To the reaction mixture, a solution of *N*-benzylacridone (**4a**, 585 mg, 2.05 mmol) and 2-adamantanone (308 mg, 2.05 mmol) in THF (15 ml) was added dropwise for 30 min and the reflux was continued for 15 h. After cooling, the reaction mixture was diluted with H_2O and extracted with AcOEt. The organic layer was washed with H_2O and saturated NaCl solution, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (CH_2Cl_2–hexane, 1:1) to give the title compound **6a** (629 mg, 76%) as colorless crystals. mp 218–219.5°C (AcOEt). IR ν (KBr): 2908, 1589, 1461, 1339, 1269 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 341 (9000), 293 (10000), 258 (17000), 226 (41000). ^{1}H NMR ($CDCl_3$) δ: 1.40–2.40 (12H, m), 3.40–3.52 (2H, m), 5.23 (2H, s), 6.82 (2H, dd, *J*=8, 1 Hz), 6.88–7.35 (11H, m). ^{13}C NMR ($CDCl_3$) δ_C: 28.1, 32.2, 37.1, 39.1–40.3 (m), 50.4, 113.5, 120.0, 120.3, 126.1, 126.2, 126.5, 126.7, 127.2, 128.5, 137.2, 143.4, 144.5. EI-MS (*m*/*z*, %): 404 (M^++H, 25). Anal. Calcd for $C_{30}H_{29}N$: C, 89.29; H, 7.24; N, 3.47. Found: C, 89.31; H, 7.32; N, 3.46.

Other olefins were prepared according to the same procedure.

3.1.2. 9,10-Dihydro-10-methyl-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6b). 74% yield, colorless crystals, mp 256–257°C (AcOEt). IR ν (KBr): 2908, 1589, 1461, 1339, 1269 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 340 (6000), 261 (15000), 226 (29000). ^{1}H NMR ($CDCl_3$) δ: 1.40–2.40 (12H, m), 3.41 (3H, s), 3.40–3.48 (2H, m), 6.98 (4H, td, *J*=7, 1 Hz), 7.15–7.26 (4H, m). ^{13}C NMR ($CDCl_3$) δ_C: 26.8–29.4 (m), 32.2, 33.3, 37.2, 38.0–41.0 (m), 111.9, 119.9, 120.3, 126.1, 126.2, 127.2, 144.2, 144.8. Anal. Calcd for $C_{24}H_{25}N$: C, 88.03; H, 7.69; N, 4.28. Found: C, 87.93; H, 7.67; N, 4.31.

3.1.3. 9,10-Dihydro-10-phenyl-9-(tricyclo[3.3.1.1^{3,7}]decylidene)acridine (6c). 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_C: 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.

3.1.4. Ethyl 9,10-dihydro-9-(tricyclo[3.3.1.1^{3,7}]decylidene)-10-acridineacetate (6d). 63% yield, colorless crystals, mp 214–216°C (AcOEt). IR ν (KBr): 2907, 1751, 1591, 1458, 1188 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 334 (7900), 286 (10000), 258 (16000), 225 (35000). ^{1}H NMR ($CDCl_3$) δ: 1.27 (3H, t, *J*=7 Hz), 1.40–2.30 (12H, m), 3.45 (2H, br s), 4.27 (2H, q, *J*=7 Hz) 4.64 (2H, s), 6.77 (2H, dd, *J*=8, 1 Hz), 6.98 (2H, td, *J*=8, 1 Hz), 7.10–7.30 (4H, m). ^{13}C NMR ($CDCl_3$) δ_C:14.2, 27.4–28.5 (m), 32.1, 37.1, 38.6–40.4 (m), 48.7, 61.3, 112.2, 119.9, 120.4, 126.0, 126.1, 127.4, 143.1, 144.7, 169.8. Anal. Calcd for $C_{27}H_{29}NO_2$: C, 81.17; H, 7.32; N, 3.51. Found: C, 80.97; H, 7.38; N, 3.42.

3.1.5. 9-Tricyclo[3.3.1.1^{3,7}]decylidene-9,10-dihydroanthracene (6e). 64% yield, colorless crystals, mp 233.5–235°C (AcOEt). IR ν (KBr): 2912, 1466, 779, 738 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 262 (16000), 234 (16000), 234 (15000), 210 (28000). ^{1}H NMR ($CDCl_3$) δ: 1.54 (1H, s), 1.50 (2H, br d, *J*=12 Hz), 1.75 (2H, br d, *J*=12 Hz), 1.88 (3H, br s), 2.09–2.22 (4H, m), 3.43 (2H, s), 3.69, 3.83 (2H, AB q, *J*=16 Hz), 7.08–7.19 (4H, m), 7.25–7.31 (4H, m). ^{13}C NMR ($CDCl_3$) δ_C: 27.6, 28.4, 33.1, 37.1, 37.7, 39.5, 40.0, 125.1, 125.2, 125.4, 126.6, 127.1, 138.7, 138.9. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.73.

3.1.6. 9-Tricyclo[3.3.1.1^{3,7}]decane-9*H*-fluorene (6f). 29% yield, colorless crystals, mp 236–237.5°C (AcOEt). IR ν (KBr): 2917, 1616, 1601, 1445 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 320 (16000), 294 (17000), 236 (47000). ^{1}H NMR ($CDCl_3$) δ: 2.00 (2H, br s), 2.10 (10H, br s), 4.07 (2H, br s), 7.20–7.35 (4H, m), 7.78 (2H, dd, *J*=7, 2 Hz), 7.88 (2H, dd, *J*=6, 2 Hz). ^{13}C NMR ($CDCl_3$) δ_C: 27.8, 35.9, 36.8,

39.5, 119.4, 124.4, 126.2, 126.7, 139.2, 139.7, 160.3. Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.71; H, 7.41.

3.1.7. 10-Benzyldispiro[acridine-9(10*H*),2′-oxirane-3′,2″-tricyclo-[3.3.1.1^{3,7}]decane] (3a). To a stirred solution of **6a** (500 mg, 1.24 mmol) was added *m*-CPBA (70%, 336 mg, 1.36 mmol) at room temperature and the stirring was continued for 15 min at the same temperature. After addition of saturated $NaHCO_3$ solution, the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with H_2O and saturated NaCl solution, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt–hexane, 1:6) to give the title compound **3a** (333 mg, 64%) as colorless crystals, mp 227–229°C (AcOEt). IR ν (KBr): 2913, 2849, 1596, 1496, 1464, 1372, 1267 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 280 (18000). ^{1}H NMR ($CDCl_3$) δ: 1.08 (2H, br d, J=12 Hz), 1.35–1.85 (9H, m), 1.95 (1H, br s), 2.10 (2H, br d, J=12 Hz), 5.27 (2H, s), 6.84 (2H, d, J=8 Hz), 6.97 (2H, t, J=7 Hz), 7.12 (2H, dd, J=8, 2 Hz), 7.15–7.32 (5H, m), 7.36 (2H, dd, J=7, 2 Hz). ^{13}C NMR ($CDCl_3$) δ_C: 26.6, 27.0, 30.0, 34.9, 36.0, 36.4, 50.3, 66.1, 96.1, 112.7, 119.9, 122.0, 125.3, 126.6, 127.0, 127.4, 128.6, 136.7, 142.9, EI-MS *m*/*z* (%): 420 (M^++H, 7). Anal. Calcd for $C_{30}H_{29}NO$: C, 85.88; H, 6.97; N, 3.34. Found: C, 85.85; H, 6.98; N, 3.30.

Other oxiranes **3b–f** were prepared according to the same procedure.

3.1.8. 10-Methyldispiro[acridine-9(10*H*),2′-oxirane-3′,2″-tricyclo[3.3.1.1^{3,7}]decane] (3b). 74% yield, colorless crystals, mp 241–242°C (AcOEt). IR ν (KBr): 2905, 2850, 1595, 1470, 1346, 1268 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 280 (14000), 214 (33000). ^{1}H NMR ($CDCl_3$) δ: 1.05 (2H, br d, J=12 Hz), 1.35–1.80 (9H, m), 1.94 (1H, br s), 2.10 (2H, br d, J=12 Hz), 3.46 (3H, s), 6.99 (4H, t, J=8 Hz), 7.25 (2H, d, J=8 Hz), 7.34 (2H, d, J=9 Hz). ^{13}C NMR ($CDCl_3$) δ_C: 26.6, 27.0, 30.2, 33.2, 34.9, 36.0, 36.4, 66.3, 96.1, 111.3, 119.8, 122.5, 125.1, 127.4, 144.1. EI-MS *m*/*z* (%): 344 (M^+, 9). Anal. Calcd for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.98; H, 7.31; N, 4.03.

3.1.9. 10-Phenyldispiro[acridine-9(10*H*),2′-oxirane-3′,2″-tricyclo[3.3.1.1^{3,7}]decane] (3c). 63% yield, colorless crystals, mp 284–286°C (AcOEt). IR ν (KBr): 2987, 2851, 1598, 1497, 1458, 1319, 1286 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 287 (14000). ^{1}H NMR ($CDCl_3$) δ: 1.19 (2H, br d, J=12 Hz), 1.40–1.85 (9H, m), 1.95 (1H, br s), 2.10 (2H, br d, J=12 Hz), 6.44 (2H, d, J=8 Hz), 6.97 (2H, t, J=7 Hz), 7.07 (2H, t, J=8 Hz), 7.37 (4H, d, J=8 Hz), 7.50–7.70 (3H, m). ^{13}C NMR ($CDCl_3$) δ_C: 26.7, 27.0, 30.2, 34.9, 36.3, 36.4, 66.0, 96.1, 113.2, 119.9, 120.4, 125.2, 127.0, 128.4, 130.6, 131.1, 140.4, 144.0. EI-MS *m*/*z* (%): 406 (M^+, 5). Anal. Calcd for $C_{29}H_{27}NO$: C, 85.89; H, 6.71; N, 3.45. Found: C, 85.98; H, 6.81; N, 3.43.

3.1.10. Ethyl dispiro[acridine-9(10*H*),2′oxirane-3′,2″-tricyclo[3.3.1.1^{3,7}] decane]-10-acetate (3d). 72% yield, colorless crystals, mp 263–265°C (AcOEt). IR ν (KBr): 2912, 2849, 1753, 1598, 1499, 1464, 1366, 1189, 1101 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 308 (5000), 276 (13000), 216 (26000). ^{1}H NMR ($CDCl_3$) δ: 1.10 (2H, br d, J=12 Hz), 1.26 (3H, t, J=7 Hz), 1.35–1.80 (9H, m), 1.93 (1H, br s), 2.10 (2H, br d, J=12 Hz), 4.26 (2H, q, J=7 Hz), 4.67 (2H, s), 6.81 (2H, d, J=8 Hz), 7.02 (2H, t, J=8 Hz), 7.20–7.30 (2H, m), 7.36 (2H, dd, J=8, 2 Hz). ^{13}C NMR ($CDCl_3$) δ_C: 14.2, 26.6, 27.0, 30.2, 34.9, 35.9, 36.4, 48.3, 61.4, 66.1, 111.6, 120.4, 122.6, 125.4, 127.4, 142.8, 169.5. EI-MS *m*/*z* (%): 416 (M^+, 37). Anal. Calcd for $C_{27}H_{29}NO$: C, 78.04; H, 7.03; N, 3.37. Found: C, 77.92; H, 7.03; N, 3.37.

3.1.11. 9,10-Dihydrodispiro[anthracene-9,2′-oxirane-3′,2″-tricyclo[3.3.1.1^{3,7}]decane] (3e). 99% yield, colorless crystals, mp 235–237°C (AcOEt). IR ν (KBr): 2913, 2850, 1608, 1447, 1351, 1147, 1097 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 264 (1000). ^{1}H NMR ($CDCl_3$) δ: 1.15 (2H, br d, J=12 Hz), 1.60 (2H, br d, J=12 Hz), 1.65–1.85 (6H, m), 1.95 (1H, br s), 2.14 (2H, br d, J=12 Hz), 3.92, 4.06 (2H, AB q, J=16 Hz), 7.18–7.25 (4H, m), 7.27–7.32 (2H, m), 7.37–7.43, (4H, m). ^{13}C NMR ($CDCl_3$) δ_C: 26.6, 26.9, 30.9, 35.3, 36.4, 36.5, 124.9, 125.4, 126.6, 126.7, 135.8, 137.5. EI-MS *m*/*z* (%): 329 (M^+, 15). Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.48; H, 7.35.

3.1.12. Dispiro[9*H*-fluorene-9,2′-oxirane-3′,2″-tricyclo [3.3.1.1^{3,7}] decane] (3f). 99% yield, colorless crystals, mp 133–134°C (AcOEt). IR ν (KBr): 2913, 2850, 1608, 1447, 1351, 1147, 1097 cm^{-1}. UV λ_{max}^{MeCN} nm (ε): 278 (12000), 214 (30000). ^{1}H NMR ($CDCl_3$) δ: 1.13 (2H, br d, J=12 Hz), 1.60–2.20 (8H, m), 2.26 (2H, br d, J=12 Hz). 2.43 (2H, br s), 7.18–7.24 (2H, m), 7.38 (4H, t, J=8 Hz), 7.73 (2H, d, J=7 Hz). ^{13}C NMR ($CDCl_3$) δ_C: 26.3, 26.8, 32.0, 35.4, 36.0, 36.4, 120.1, 124.0, 126.2, 128.4, 140.8, 141.9. EI-MS *m*/*z* (%): 315 (M^+, 41). Anal. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.72; H, 7.38.

3.2. Typical procedure for the measurement of chemiluminescence of the oxiranes 3

Alkaline hydrogen peroxide (0.1 M H_2O_2 in 0.1 M aqueous NaOH solution, 0.10 ml) was added to a DMSO or dioxane solution of the oxirane **3** (1.0×10^{-7} M, 0.10 ml). DMSO, which can dissolve all the oxiranes **3a–f**, was employed to study the structural effect on the chemiluminescence (Table 1). Dioxane was employed to investigate the effect of the kind of acid used (Figs. 2–6) because **3a** in dioxane showed the strongest light emission. After a certain period of time (25 s for the addition of HCl and 60 s for the addition of the other acids), an aqueous solution of the acid (0.2 M, 0.10 ml) was added to the reaction mixture. Light emission was immediately monitored for 120 s on a photon counter.

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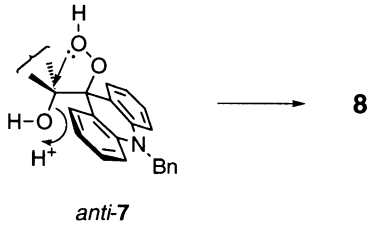

Figure 8. Formation of dioxetane **8** from *anti*-**7**.

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